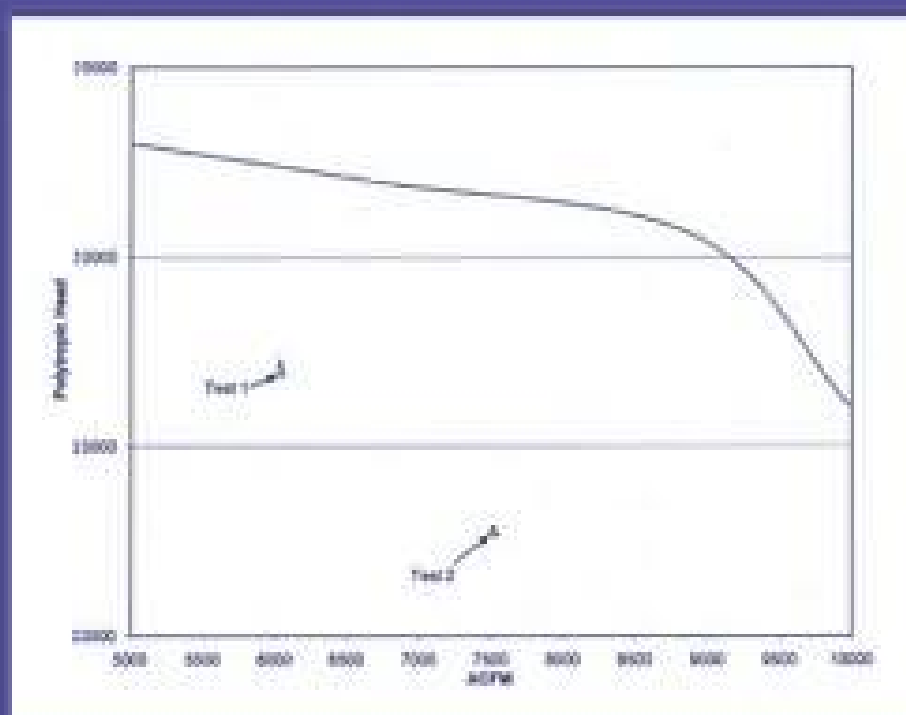


PROCESS ENGINEERING PROBLEM SOLVING

Avoiding “The Problem Went Away,
but it Came Back” Syndrome



JOE M. BONEM

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 **WILEY**

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This book is an attempt to both leave a legacy and to provide assistance for those starting or in the early stages of a career in engineering.

The efforts in putting this book together are dedicated to:

My Wife, Diane, who managed to teach me through words and examples that “people are more important than things”.

Our Children, Mike, Tracey and Amy, who during their teenage years, taught me the value of just listening rather than always trying to solve problems.

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PREFACE

The subtitle of this book comes from my experience of listening to frustrated engineers describe problem solving in modern complex process plants. I have often heard the expression—“We did a couple of things and the problem went away”. As I heard this, I normally said either to myself or aloud—“If you don’t know why it went away, there is a high probability that it will come back”.

During years of experience, I observed well-trained chemical engineers that had graduated in the upper part of their class having difficulty solving plant technical problems. I concluded that often these well-trained engineers were not really trained in subjects that would allow them to solve real-life plant process problems. They had minimal training in problem-solving techniques and much of their academic training was not directed at pragmatic solutions. For example, the academic world was training in thermodynamics, but not in how does the theory apply to reciprocating or centrifugal compressors. With this limited amount of training in approaching real-world problems, the process engineer would often settle for a problem-solving approach based on logic with no calculations or even worse simple intuition. In addition, the pressures of a real-life problem-solving environment often caused him/her to take the approach of “trying something even if it doesn’t work”. Management rarely indicated that the engineer should take the time to make sure that the problem was worked correctly. Many times the belief of an operator and/or mechanic was taken as being the correct problem solution simply because the engineer did not have a good framework to develop any other possibility. Since the graduate engineer and operator now seemed to agree, management felt comfortable in implementing the “joint recommendation”. Often times these solutions failed. Even worse, the results of the attempted solutions were not documented and there was a strong possibility that the same problem solution would be tried again at a later date.

In an effort to mitigate the failure to solve industrial problems, a new series of techniques were developed that called for using teams to solve problems via interactive “brainstorming” approaches. I observed that the advantages of these teams were that they often brought a tremendous amount of data to bear on the problem and that they generated a long list of *possible* hypotheses.

However, this approach was no more effective than the previous ones. The reason why this large amount of data failed to produce effective solutions was that there was no systematic analysis of the data. In addition, there was no stipulation that the possible hypotheses had to be theoretically possible. Thus, theoretically impossible hypotheses were treated with the same validity as the theoretically possible ones. The most likely outcome of such brainstorming sessions was that the solution with either the most votes or the loudest proponents was adopted as the recommended approach.

In spite of these less than perfect approaches, industrial problems are being solved by intuitive, logical approaches and/or brainstorming that do not involve calculations and/or data analysis. Most of these problems are being solved by experienced engineers and/or operators. However, these problems are generally not complex or chronic in nature. It is the chronic problems and/or those requiring an engineering analysis that this book addresses. In addition to the current situation, as the “baby boomers” age and retire, the experience that is often of value in problem solving is not being replaced. Thus, a more structured approach will become even more important in the next decade.

I cannot claim that the techniques discussed in this book will allow the process engineer to achieve perfection in the area of problem solving. However, I can say that these techniques have worked for me throughout a long career of industrial problem solving. The chemical engineering fundamentals discussed in the book are presented from the perspective of the problem solver as opposed to the perspective of a process designer or the perspective of one in the academic world. There are shortcuts and simplifying assumptions that are used. These may not be theoretically precise, but they are more than adequate for problem-solving activities. There are without a doubt additional chemical engineering fundamentals that should be covered. However, I have selected those areas that I felt would be of most value to the industrial problem solver.

My industrial experience indicates that there are three requirements to successfully solving complex problems. They are as follows:

1. You must have verifiable data.
2. You must use a structured problem-solving approach that includes a statement of what problem you are trying to solve. This requires rigid discipline. As discussed in Chapter 1, we often fail at simple problem solving because we tend to rely on intuition or experience-based solutions as opposed to a more rigorous structured problem-solving approach.
3. You must use sound engineering skills to develop a *simple* working hypothesis.

If any one of these three is absent, unsatisfactory results will likely result. For example, a logical solution to a problem is of no value if it is not based on

sound data or if the conclusion violates a fundamental premise of engineering. Conversely, a sophisticated computer simulation program is of little value unless it is directed toward solving the correct problem.

Multiple surveys and interviews throughout the United States have listed “problem-solving skills” and “vocational-technical skills” in the top 10 skills that employers wish their employees had. This book deals with these two skills as follows:

1. The three essential problem-solving skills (Daily Monitoring System, Disciplined Problem-Solving Approach, and Determining Optimum Technical Depth) are discussed and guidelines are provided for successful implementation of each of these.
2. Vocational-technical skills are enhanced by equipment descriptions, helpful hints and practical knowledge that will expand the problem solver’s academic training. The helpful hints and practical knowledge include calculation techniques that are presented without lengthy derivations and proofs.

Several example problems are included throughout this book in order to illustrate the concepts and techniques discussed. Some of the example problems are included in the chapters devoted to specific aspects of process engineering. The remainder are included in Chapter 13. This chapter is meant to deal with a series of problems that involve multiple aspects of process engineering problem solving. The problems in the book are for the most part real-world problems. The failures and successes described actually occurred. The problem-solving techniques described in this book were responsible for the successes. Failures were often due to not using the techniques described. Occasionally, fictitious problems are created to help illustrate important concepts or calculation techniques.

The English set of units has been used throughout the book. The English units and their abbreviations are described at the end of each chapter. A table of conversion factors to scientific units is provided in Appendix 2.

Throughout the book, I have used the term “problem solver” to mean the individual with direct responsibility for solving the problem under consideration. I have also used the masculine pronoun “he” knowing full well that there are talented female problem solvers as well.

I have often been asked about the utilization of the principles described in this book by other engineering disciplines or by operators/mechanics. It is my firm belief that the problem-solving principles (Daily Monitoring System, Disciplined Problem-Solving Approach, and Determining Optimum Technical Depth) described in this book could be used by other engineering disciplines or operators/mechanics. A non-process engineer could not be expected to have the academic skills to formulate a full range of process hypotheses. However, he will have the skills to formulate hypotheses associated with his

particular discipline. In addition, because of the pragmatic approach used in the book, it is likely that a non-process engineer or an operator/mechanic could readily learn how to do the calculations required to formulate some theoretically correct hypotheses.

Joe M. Bonem

INITIAL CONSIDERATIONS

1.1 INTRODUCTION

Problem solving is an area that is found throughout all activities of daily life. Problem solving tends to take place in two mind modes. There is the intuitive or instinctive reactionary mode, which has also been called “gut feel”. Then there is the methodical reasoning approach, which is usually based on theoretical considerations and calculations.

Either of these approaches has its place in real-world problem-solving activities. The intuitive reactionary person will respond much faster to a problem. The response is usually based on experience. That is, he has seen the same thing before or something very similar and remembers what the problem solution was. However, if what is occurring is a new problem or is somewhat different, his approach may well lead to an incorrect problem solution. The methodical reasoning person will not be able to react to problems quickly, but will usually obtain the correct problem solution for complicated problems much faster than the intuitive reactionary person who must develop several aborted “gut feel” solutions.

An example of how two people with these different mind sets will react can be found in the most unlikely places. For example on a golf course, the cry of “Fore” will illicit different responses. The person responding based on intuition or instinct will immediately cover his head and crouch. This will reduce the probability that the errant golf ball hits a sensitive body part. The person responding based on methodical reasoning will begin to assess where the cry

came from, where the ball might be coming from and reach a conclusion where it might land. Obviously in this case, reacting based on intuition or instinct is a far superior mode of operating. There could be many more examples from the sports world where reacting in an intuitive fashion yields far superior results than reacting in a methodical reasoning manner. *However*, essentially all of these examples will be experienced based. People that are reacting successfully in an intuitive mode know what to do because they have experienced the same or very similar situations.

Similar things happen in industrial problem solving. Experienced people (engineers or operators) react instinctively because they have experienced similar events. These operators or engineers do an excellent job of handling emergency situations or making decisions during a start-up. As a rule, the person that tends to respond based on methodical reasoning and calculations rarely can react fast enough to be of assistance in an emergency or if quick action is required in a start-up situation. The exception to this rule is the engineer that has designed the plant and has gone through calculations to understand what will happen in an emergency or start-up. In effect, he has gained the experience through calculations as opposed to actual experience.

The experience necessary to conduct problem solving in the real world does not always exist. In addition, while the need for quick response when solving industrial problem is real, there is not always an emergency or crisis need to take immediate action. Thus, the methodical reasoning approach is often the desirable mode of operating. The three components of this methodical reasoning approach are:

1. A systematic step-by-step procedure. This includes the three essential problem-solving skills (Daily Monitoring System, Disciplined Problem-Solving Approach, and Determining Optimum Technical Depth).
2. A good understanding of how the equipment involved works.
3. A good understanding of the specific technology involved.

Before discussing problem solving in industrial facilities, two examples from everyday life are discussed. It often aids learning, to discuss things that are outside the scope of the original thrust of the teaching. The two examples from everyday life discussed below will be helpful in understanding the difference between intuitive problem solving and those based on methodical reasoning.

1.2 AN ELECTRICAL PROBLEM

While trimming bushes with an electric hedge trimmer, a laborer accidentally cut the extension cord being used to power the trimmer. He had been using

an electrical outlet in a pump house located approximately 70 feet from the main house. The only other use for 110-volt electricity in the pump house was for a small clock associated with the water softener. The laborer found another extension cord and replaced the severed cord. However, when he plugged it in and tried to turn on the hedge trimmer, it did not have any power. He then had to report the incident to the homeowner. The homeowner checked the panel mounted circuit breakers. None of them appeared to be tripped. However, to be sure he turned off the appropriate circuit breaker and reset it. However, power was still not restored to the outlet in the pump house. To make sure that the replacement extension cord was not the problem, the homeowner plugged another appliance into the electrical outlet in the pump house. It did not work either. The homeowner then concluded that the electric outlet had been “blown out” when the cord was cut. He replaced the electric outlet. However, this still did not provide power to the equipment. When the homeowner rechecked the circuit breaker, he noticed that a GFI (Ground Fault Indicator) in a bathroom was tripped. Resetting this GFI solved the problem.

While the homeowner believed that in this particular house every GFI protected a single outlet, it is not unheard of to protect more than a single outlet with a GFI. It seemed surprising that the GFI in a bathroom also protected an outlet in the pump house 70 feet away. The homeowner then recalled that at some point in the past, he had noticed that the small clock in the pump house was about 2 hours slow. This clock was always very reliable. In retrospect, he remembered that at about the same time that the clock lost 2 hours, this particular GFI had tripped during a lightning storm and had not been reset for a few hours. Thus, it became obvious that the accidental cutting of the extension cord had caused the GFI to trip rather than tripping the circuit breaker or “blowing out” the electrical outlet. The failure to correctly identify the problem cost the homeowner a small amount of money for the electrical plug and a significant amount of time to go to town to purchase the plug and then install it.

Note that the homeowner’s intuitive approaches were all real possibilities. That is, the circuit breaker could well have tripped, the replacement extension cord could have had an electrical break in it, or the electrical outlet could have failed when the original extension cord was cut. His problem solving just did not go into enough detail to solve the problem quickly. Several lessons can be learned from this experience. While it seemed to be a simple problem that could be easily solved based on the homeowner’s experience, the intuitive approach did not work. A more systematic approach based on methodical reasoning might have improved results as follows:

- Consideration would have been given to the possibility that GFIs can protect more than one plug. The distance between the GFI and the electrical outlet would not be a consideration. The homeowner did not fully understand the technology.

- A voltmeter would have been used to check that power was available coming to the electrical outlet. If power was not available coming to the outlet, the “blown plug” hypothesis would be invalid. A systematic approach was not used.
- In addition, a systematic approach would have raised the question of whether the clock losing 2 hours could be related to the lack of power at the electrical plug.

1.3 A COFFEEMAKER PROBLEM

A housewife experienced problems with a coffeemaker overflowing about half of the time when she made either a flavored or decaffeinated coffee. The coffee and coffee grounds would overflow the top of the basket container and spill all over the counter. The coffeemaker performed flawlessly when regular coffee was used. A sketch of the coffeemaker is shown in Figure 1-1. When the coffeemaker is started, water is heated and the resulting steam provides a lifting mechanism to carry the mixture of water, steam and entrained air into the basket where the ground coffee resides. The hot water dissolves the coffee and it flows into the carafe. The coffeemaker is fitted with a cutoff valve that causes the flow out of the basket to stop if anyone pulled the carafe out while coffee is still being made.

The housewife asked her husband, a graduate engineer, to determine what was wrong. The housewife’s engineer husband examined the problem by first convincing himself that his wife was following directions when it came to making the coffee. He then carefully examined the equipment especially the

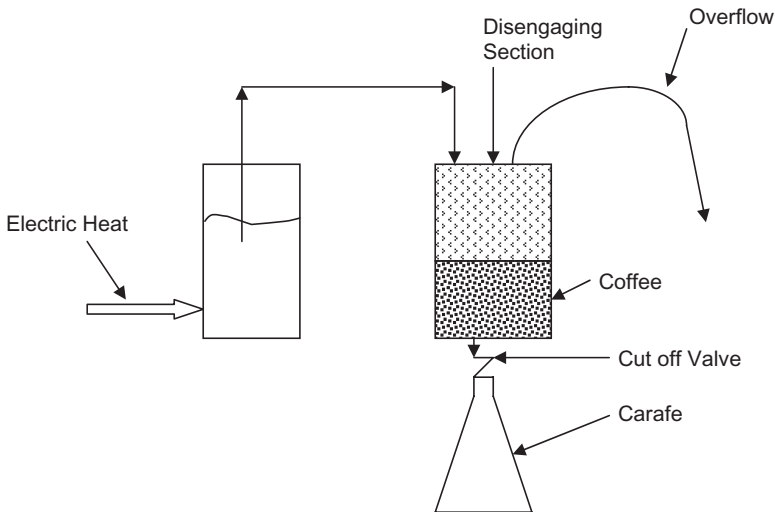


Figure 1-1 Coffee pot schematic.

cutoff valve. He concluded that somehow the cutoff valve was restricting the liquid flow whenever decaffeinated or flavored coffee was being made. That is, the incoming flow of hot water and steam was greater than the flow out of the valve. This would cause the level in the container to build up and run over. The problem solution seemed relatively simple. He removed the valve and made a sign that said “Do not remove carafe until coffee is finished brewing”. He felt a surge of pride in not only solving the problem, but that he prevented a future problem by providing instructions to prevent someone from pulling out the carafe. The next time that one of the suspect coffees was made, the container did not overflow. He then announced that the problem was solved.

Unfortunately, the glow of successful problem solving did not last long. The next time that flavored coffee was made the problem reoccurred—that is, the coffee and grounds overflowed the top of the basket container. The engineer then began a more detailed investigation of the problem including understanding the technology for making flavored and decaffeinated coffee. He discovered that when decaffeinated coffee was being made, a surface-active material was utilized. This surface-active material was mixed with the coffee to extract the caffeine. He extrapolated from this and theorized that when flavored coffee was being made, a surface-active material was used to evenly distribute the flavor to the coffee. Once he understood the difference in the coffee-making processes, he theorized that residual amounts of the surface-active material being left on the coffee reduced the surface tension of the hot water and coffee, and allowed it to foam up in the container and out over the sides onto the counter.

Since the amount of residual surface-active material would vary slightly from batch to batch, it was theorized that only the batches of either flavored or decaffeinated coffee that contained greater than a critical level would cause an overflow. After studying this theory, the engineer decided that the problem solution would be to obtain a coffeemaker that had a basket container with a different design. The problem coffeemaker had a small cylindrical shaped basket. A new coffeemaker with a large conical design basket was purchased. The comparison of the two baskets is shown in Figure 1-2. It was theorized that the large conical design would provide a reduced upward velocity of the foaming material and this would allow more disengaging of the vapor trapped in the foam. The purchase of this coffeemaker eliminated the problem completely.

Several lessons can be learned from this problem-solving exercise. The intuitive hunch that coffee was not flowing through the valve as fast as hot water was coming into the basket made logical sense. However, no logical explanation was provided for why this only happened with flavored or decaffeinated coffee. Any theory that has the phrase “for some reason” is suspect and is an indication of an incomplete problem analysis. An incomplete problem analysis almost always has a portion of the analysis that is very logical. However, it is imperative that the entire analysis be logical. Another error was

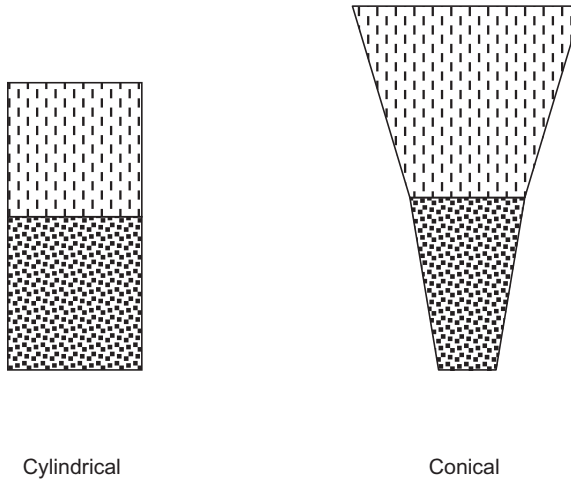


Figure 1-2 Basket comparisons.

that in formulating the hypothesis, the engineer assumed that only liquid water and solid coffee existed in the container. He overlooked the fact that steam vapors and entrained air were always carried into the container with the hot water. The presence of steam and air would provide a mechanism for creating a frothy mixture. The example also illustrates the need for the following:

- A systematic approach—A systematic approach as will be described later in this book would have eliminated the incomplete hypothesis that suggested the outlet valve was a restriction on only certain grades of coffee.
- A good understanding of how the equipment works—If the engineer had understood how the coffeemaker worked, he would not have assumed that only a liquid was present along with the coffee in the container. He would have recognized that both steam and air were carried over into the container along with the hot water.
- A good understanding of the technology involved—The fact that decaffeinated and flavored coffee performed differently than regular coffee should have been an indication to the engineer that he needed to examine the difference in the coffee-making technology.

These relatively simple examples of how successful problem solving requires a more detailed analysis than simple logic and/or intuition are meant to set the stage for the next chapter which deals with limitations to industrial problem solving. While industrial problems are almost always more complicated than those described in this section, the same problem-solving approach needs are present.

LIMITATIONS TO PLANT PROBLEM SOLVING

2.1 INTRODUCTION

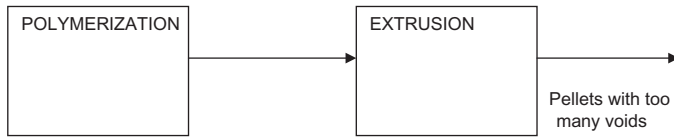
While later chapters will consider the engineering approach to problem solving, any book dealing with plant problem solving will touch on the question—“Is problem solving really engineering?” If one defines engineering as dictionaries do—“The science of making practical application of knowledge in any field”, we must conclude that problem solving is truly engineering. Often engineers may conclude that problem solving is not truly engineering because of the following:

- Engineering is defined in such narrow terms that only “design work” appears to be engineering.
- Intuition and “gut feel” have replaced thorough analysis as a preferred tool for problem solving.
- Considerations of “optimum technical depth” are not well understood.

It is also important to understand why a course in engineering problem solving is of value. In a typical industrial problem, a customer is unhappy with the appearance of the plastic pellets being received from his supplier. Specifically, the pellets have visual discontinuities that he describes as “voids”. A simplified statement of the problem is shown in Figure 2-1.

As shown in this figure, the process where the pellets are manufactured consists of two sections (polymerization and extrusion). A strong correlation

PROCESS



CORRELATION

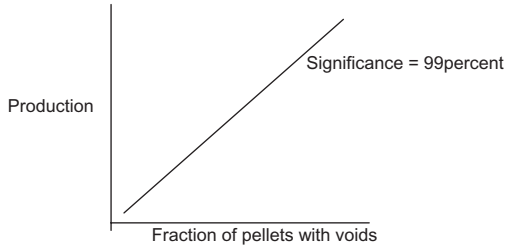


Figure 2-1 An example of improper problem solving.

was developed between the pellet appearance (fraction of pellets with voids) and the polymerization production rate. The problem solver recommended that the production rate be reduced to solve the “multi-void” problem. The solution to the problem (reducing production rate) is at best only a short-range solution. This solution cannot be considered a lasting solution because of the following:

- The basic cause of the voids was not considered.
- The solution required a severe economic penalty (It might have worked one problem, but it created another one). In most process industries, the limited profits are made at production rates above 75 or 80 percent of capacity.
- Since the basic cause of the voids was not discovered, the problem will likely reoccur even at the reduced production rates.

2.2 LIMITATIONS TO PROBLEM SOLVING

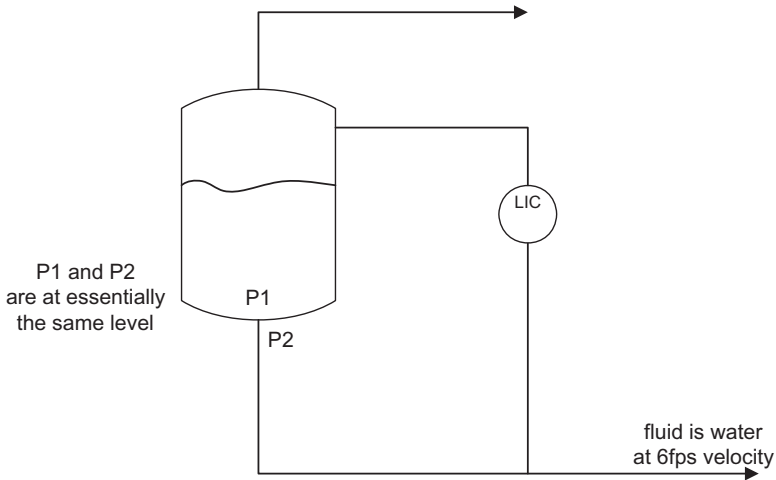
The previous example is typical of much of the improper problem solving that occurs in many industries in today’s hectic fast-paced society. It also illustrates why a course in engineering problem solving is of value. There are 10 primary limitations to problem solving in today’s process plants. They are described as follows.

1. Modern day process plants are large and complex. For example, a relatively simple process such as propylene purification has evolved from fractionation followed by a drying process to remove water to a process incorporating “heat pump fractionation” and more complicated conversion steps to remove impurities to the ppb level. In addition, the plant sizes have increased significantly. Thus, there is even more emphasis on solving problems quickly and correctly. There does not seem to be any change in either of these trends.
2. The problem is usually more complicated than first described. Typical initial problem descriptions might consist of such statements as “It won’t work as designed” or “It won’t work unless you modify it to ...” If either of these problem descriptions is accepted exactly as stated, the engineer is doomed to failure. In order to practice true engineering problem solving, the engineer must use a disciplined approach that involves *writing out* an accurate description of the problem that *does not* include a problem solution. This is necessary to avoid ignoring data and jumping to conclusions.
3. Conflicting data are always present. This can take many forms. Some examples are verbal description of eyewitnesses can disagree, laboratory data may be in disagreement with physical factors, instrumentation or even other laboratory data, and/or instrumentation/computer data may be in conflict with other sources of data.
4. Modern day plants have a high degree of variable interaction. This results in difficulty in isolating the real problem causing variable, and/or strong correlations between dependent variables. (While this may be of interest, it rarely results in solving problems.)
5. Besides a high degree of variable interaction, there is also a high degree of interaction between the various engineering disciplines. Thus, what appears to be an obvious mechanical engineering problem often has its true roots in chemistry and/or chemical engineering. The converse is also true.
6. System dynamics involve long holdup times. In the modern day process, there is usually an incentive to “push the process” to higher efficiency or higher purity. This usually leads to longer residence times in equipment. Problem solving with long residence time equipment requires the use of a dynamic model. Unfortunately when faced with the need for a dynamic model, the problem solver will often take one of two unsatisfactory approaches. He will give up on the basics and say “It’s too complicated”. Since the dynamic model is truly required to solve the problem, the problem solver now must take an approach that can be characterized as “guesswork”. The other extreme is that he will begin the development of an elaborate technically correct model that will rarely be finished in time to be of any assistance. Either of these approaches overlooks the fact that there are ways to build simple

technically correct dynamic models. These simple models will contain assumptions. However, these assumptions will still provide a model with sufficient accuracy to solve industrial problems.

7. Engineering principles are often inadequately applied. In today's industrial environment, pressures to perform at a minimum cost and manpower commitment often encourage "shooting from the hip" as a problem-solving technique. This may be completely appropriate in some limited situations. However, the purpose of this book is to address the chronic problem that is only wounded by the "shoot from the hip" technique. The modern chemical engineering curriculum, while providing an excellent theoretical foundation, often fails to adequately stress application of fundamentals. For example, Bernoulli's theorem can be used to explain inaccurate values from the poorly designed level instrument shown in Figure 2-2.
8. There is often failure to use a methodical approach. While this limitation is closely allied with the previous one, it points out a need to structure even the best application of engineering principles. This structuring step is necessary to allow one to define which of the engineering principles are most appropriate. The failure to use a methodical approach could lead one to hypothesize erroneously that a fractionating tower had a plugged tray and that was the cause of the high-pressure drop. In fact, the problem might well be associated with a change in internal vapor and liquid loading, buildup of an impurity that boils between the light key and heavy key, foaming caused by a trace impurity, or improper assumptions regarding tower loading point.
9. The whole picture is often not seen. The problem solver that fails to use a methodical approach is vulnerable to arriving at the wrong answer because he fails to see the whole problem. There are often verbal clues that the problem solver is failing to see the whole picture. Some of these clues are comments such as "That's a mechanical problem" or "The laboratory is wrong again". While these statements may be valid; they are often indications that the problem solver is excluding essential pieces of data. It should be noted that someone using the methodical approach is less vulnerable, but still subject to this limitation.
10. There is often an overdependence on history. While a historical database is a mandatory prerequisite for successful problem solving, the database should be used to define deviations rather than a repository of answers. The statement "The last time that this happened, it was due to. ..." must always be tested by data analysis.

As described earlier, Figure 2-1 shows a typical industrial problem. Several of the limitations discussed above are apparent. The problem was certainly complex in that it could be caused by conditions in either the polymerization or the extrusion area. There appears to be both a lack of a methodical approach



Connecting the level instrument in the process line as shown will result in the measured level reading being 0.5 feet lower than actual.

This is based on Bernoulli's theorem

$$dP/D + dV^2/2g + dZ = 0$$

where

dP = difference in pressure

D = density of liquid

dV² = difference in liquid velocities squared

g = gravitational constant

dZ = difference in liquid height

At base level the pressure at the level instrument will be less than the same pressure in the drum as follows:

$$(P2-P1)/62.4 + (36-0)/64.4 = 0$$

$$P1-P2 = 34.9 \text{ lbs/feet squared}$$

this is equivalent to 0.5 feet in measurement of level

this ignores the friction loss in the line and nozzle

Figure 2-2 Example of improper level instrumentation.

and an inadequate application of engineering principles. In addition, while only a limited amount of data is present in Figure 2-1, the problem solution appears to be only historically based. There is no evidence that a hypothesis was developed and tested with a plant test. Was the problem solver seeing the entire picture? For example, was the independent variable polymerization production rate or extrusion rate? Was the independent variable production rate or residence time (the inverse of production rate)? Perhaps the confusion of the problem solver is illustrated by the figure, which shows the “voids” on the x -axis, which is normally reserved for the independent variable.

SUCCESSFUL PLANT PROBLEM SOLVING

3.1 INTRODUCTION

Before beginning a discussion on how one conducts successful engineering problem solving, perhaps a definition of the activity is appropriate. Engineering problem solving is defined as the application of *engineering principles* to allow *finding*, *defining*, and *solving* plant-operating problems in an expedient and complete fashion. The *finding* and *defining* phases of problem solving are often ignored, considered obvious, or unimportant. However, these phases prevent small problems from growing into large problems and allow the problem-solving phases to be done in an expedient fashion. Finding the problem involves sorting through the mass of laboratory and process data to uncover deviations that may only be 1 sigma from normal, but which have the potential to grow into large deviations. Defining the problem involves developing a quantitative description of the problem specifications.

Successful engineering problem solving will always involve the following:

- A *daily* monitoring system
- A *disciplined* (not intuitive), *learned* (not inherited) engineering problem-solving approach
- The ability to distinguish between problems requiring technical problem solving and those only requiring an expedient answer. The ability to determine how detailed a technical analysis should be is also required to

efficiently solve plant process problems. This is referred to later as *optimum technical depth*.

3.2 FINDING PROBLEMS WITH A DAILY MONITORING SYSTEM

In order to successfully find and define problems, the problem solver must obtain and maintain a historical database. The database can be maintained by using several different sources. The *Managerial Objective* will also be important. The *Managerial Objective* is defined as goal that management has defined for the particular process. This goal will vary depending on the age of the process, technical staffing of the location and the value added by the process to name a few. Table 3-1 shows a grid of both *Managerial Objectives* and sources of data.

As an example in the use of this table, assume that a well-established process is producing a commodity chemical. As a general rule, commodity chemicals have a low value added. That is, the difference between the product revenues and the cost of production is very small. Management might elect to staff so that the technical organization could only respond to established significant problems. Thus, the *Managerial Objective* might be characterized as Minimizing Routine Work and Maximizing Variable Retention. In this case, the number of process variables to be retained would be maximized. As shown in Table 3-1, Computer Data Storage would be the desired source of data to fit this objective. If a problem developed, the problem solver could then go

Table 3-1 Sources of historical data

Source	Managerial Objective				
	Minimize Routine Work	Maximize Finding Hidden Problems	Maximize Trend Spotting	Maximize Variable Retention	
				Volume	Key ⁽¹⁾
Computer data storage	X			X	
Computer or hand graphs			X		X
Delta data graphs ⁽²⁾		X	X		X
Communication with hourly workers		X			
Visual observation of field equipment		X			

(1) The concept of key variable retention involves retaining the graphs or delta data graphs of only the key variables, whereas volume retention involves a data source that relies on maintaining values of every variable.

(2) "Delta Data Graphs" are the difference between actual values and a theoretical or established value. An example of such a plot is shown in Figure 3-1.

back and use the stored data to attempt to resolve the problem. He might find this difficult due to the vast amount of data that must be analyzed. In addition, the data sources entitled Communication with Hourly Workers and Visual Observation of Field Equipment would likely not be available since people's memory might have faded and changes might well have occurred in the field equipment.

On the other hand, if the process being considered is an unproven process and/or is a high value-added process, management might elect the objective of Maximize Finding of Hidden Problems. In this case, the problem solver would use Delta Data Plots, Communications with Hourly Workers and Visual Observations of Field Equipment as his data sources. It is likely that the main source of historical data would be the trend graphs or delta data graphs. Of course in this case, the computer would still be used to store all process variable data. However, it would not be the primary source of data for the problem solver. While this objective allows for finding problems quickly, it likely will require more technical staffing.

In the two cases cited above there are implicit assumptions. In the case where the *Managerial Objective* is Minimizing Routine Work and Maximizing Variable Retention, the implicit assumption is that essentially all process problems that occur can be readily solved without a detailed problem analysis. In the case where the *Managerial Objective* is Maximize Finding of Hidden Problems, the implied assumption is that essentially all problems will require a detailed problem analysis.

If graphs are to be used in any of the cases shown in Table 3-1, they should be drawn, reviewed and monitored on a daily basis. To monitor the process by preparing these graphs only once a week defeats the purpose of finding problems or spotting trends.

This daily monitoring system should be designed to allow the problem solver to monitor process variables by incorporating several variables into process models that summarize the operation of each section of the process. An example of this is shown in Figure 3-1. In this figure, reaction kinetics are expressed as a percent of theoretical. Significant deviations from 100 percent are indicative of process impurities, catalyst contamination or inaccurate process measurements. Thus with only a glance at the figure, it is possible to assess the status of the reactor section of the process.

Even a cursory look at Figure 3-1 will raise the question of when does the problem solver declare that a problem has occurred. Is it the first drop in kinetics or the second? For each variable that is graphed, there should be a limit that if the actual value goes above or below will indicate to the problem solver that it is likely that a problem is occurring. This will be discussed later and is referred to as the concept of a "trigger point".

One source of historical data requiring elaboration is discussions with Operating, Mechanical and Laboratory hourly personnel. Their observations may be highly subjective but at the same time very meaningful. For example, discussions with laboratory personnel revealed that a standard Millipore filter

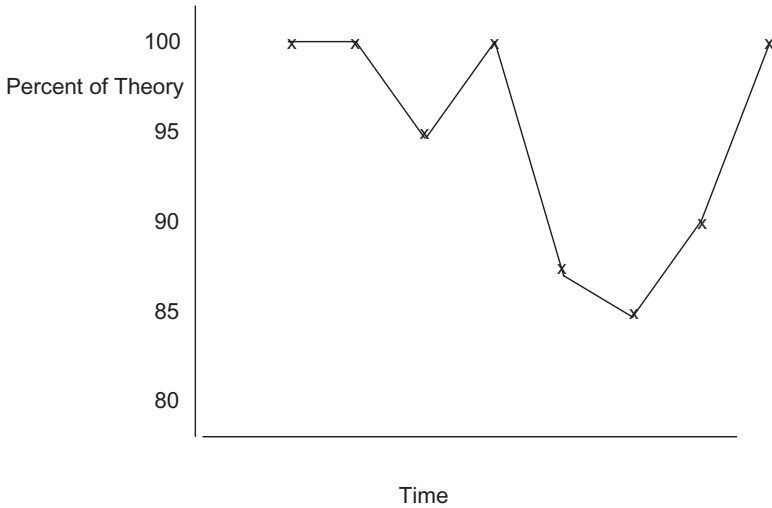


Figure 3-1 Essential variable (reaction kinetics) percent of theory versus time.

test used to determine the level of solids contamination in a hydrocarbon caused “fusing” (melting together of the two parts) of the Millipore filter container. This plastic container was known to be inert to the hydrocarbon and “fusing” had never been encountered before. Based on the laboratory technician’s comment that the container was “fusing” an investigation was initiated. This investigation showed that the hydrocarbon was contaminated with methanol. The plastic used in the Millipore apparatus was soluble in methanol. Small amounts of methanol would cause the melting point to be reduced and the “fusing” of the two parts of the container. The determination that the hydrocarbon was contaminated with methanol provided a strong clue for developing a hypothesis for determining the source of the known hydrocarbon contamination.

In this day and time with the multiple means of “nonpersonal” data acquisition techniques, the communications flow from hourly workers to professionals must be cultivated and nourished primarily by the professional.

The observation of field equipment is done by walking through the process plant and both looking at and listening to the equipment to detect any differences since the last walk-through. For example, a loud noise that appears to be emanating from a process vessel might be indicative of condensation of vapor inside of the drum. A problem solver on a walk-through may observe a new sample connection, which on closer examination may appear to be installed in such a fashion that it will not give a representative sample. These observations by themselves may not be problems, but they are sources of data that can be considered as other problems are detected. The problem solver should make notes on anything that seems different. These notes will provide data with a time stamp that can be used for future references.

It is inadequate to only record data and collect observations. The examination of the data can best be done with “trigger points”. “Trigger points” are limiting values of either laboratory analyses, instrument readings or computed variables. If the variable being monitored is outside of these limits, the *successful* problem solver will declare that a problem exists and begin to solve the problem. It should be emphasized that the *successful* problem solver will *find and define* the problem well before it becomes a major problem. The finding and defining the problem is the first step toward problem resolution. Resources may not be available to resolve the problem completely; however, management will recognize that a problem has been uncovered. The “trigger point” approach is similar to that used by the medical profession. Medical and laboratory tests such as blood pressure, cholesterol level and hemoglobin levels are used to spot minor problems before they become major problems.

One of the most important things to recognize in setting trigger points is that there is a difference between using statistics to control a process and using statistics to find problems. Control statistics require that the process be greater than 3 sigmas from target before changes are made. This implies that there is a 99+ percent confidence level that there has been a real change in the process as opposed to process variability. The successful problem solver cannot wait until he is 99+ percent confident that there is a process problem. For example, very few car owners wait until they are 99+ percent confident that they have an automobile problem before they begin a problem-solving activity.

Trigger points can be set for the following different types of variables:

- Theoretical/Laboratory/Pilot Plant Demonstrated—Each of these variables would have a “lumped parameter constant” (to be discussed later) that can be calculated from plant data. These constants can then be compared to similar constants demonstrated in the laboratory or pilot plant or that can be developed from theory. Examples of these are reaction rate constants (demonstrated in the laboratory or pilot plant), or fractionation tower tray efficiencies (demonstrated by theoretical calculations).
- Plant Demonstrated—These include variables that are equipment related such as production, purity, slurry concentration or additive controllability. They can only be demonstrated in a commercial size plant where full-scale equipment is utilized.
- Vendor Demonstrated or Guaranteed—These will be almost exclusively equipment items. These variables will include items such as highly specialized valves, volatile removal equipment, or heat exchange equipment.

Statistical techniques can be utilized to set “trigger points”. For example in a process demonstrated to have a catalyst efficiency of 5000 with a one sigma of 200, a low “trigger point” of 4900 would be ludicrous. Conversely, a “trigger point” of 4400 would cause many problems to be ignored. Obviously, determining a meaningful standard deviation is mandatory if the “trigger point approach” is to be utilized.

It is highly likely that in an industrial process, the standard deviations of essential variables are not well known. Rather than doing elaborate laboratory statistical studies, a more expedient approach will involve developing approximate standard deviations and allowing the daily process monitoring to help determine the real commercial standard deviation.

In a new process, there is great value in setting the standard deviation on the low side and attempting to explain as many deviations as possible. The tightening of the standard deviation for a new process will cause the maximum number of problems to be uncovered while management's attention is focused on getting the new process operational and adequate resources are available to solve problems. The opposite approach of having a large standard deviation will result in an apparent good start-up followed by a multitude of problems 6 to 12 months later. These problems that occur in 6 to 12 months were actually present during the start-up as small problems that went undetected due to the large standard deviation being utilized.

While problem solvers generally think in terms of negative deviations (failure to achieve a target), positive deviations must also be considered. For example, a critical heat exchanger that had a known heat transfer coefficient of 120 ± 10 BTU/hr-ft²-°F suddenly began operating with a coefficient of 150. An investigation is warranted to determine what had happened to cause an apparent new baseline. This investigation of positive deviation will often lead to new and improved operating procedures.

While the actual setting of trigger points depends on the process as well as the individual company, Table 3-2 shows some suggested ones. It should be recognized that each of these is based on a statistical approach once a standard deviation has been developed or approximated.

In summary, the key concepts in the use and the defining of trigger points are:

- They should be based on statistics and theoretical values where possible.

Table 3-2 Suggested trigger points

Magnitude of Variable on Profits	Trigger Point, Sigma	Probability of Type 1 Error ⁽¹⁾ , Percent
Very significant (or new process) ⁽²⁾	1	30
Moderate	2	5
Insignificant	3	<1

(1) A type 1 error is the probability that a problem would be declared when no problem really existed. For example, if the trigger point criterion is set at 1 sigma, there is a 30 percent probability that a declared problem is really just a normal fluctuation in the process. *However*, there is a 70 percent probability that a real problem exists.

(2) Items that could cause a very serious upset (plant shutdown) should be evaluated using a *one-sided* test against a criterion of being 60 percent or less sure that you are right. Thus, a trigger point of only 0.3 sigma could be important.

- The criterion for declaring that a problem exists is different from the criterion for taking control action.
- The criterion for declaring that a problem exists will be a function of severity of the problem. In addition, the point on the learning curve for specific process should be considered.
- Positive deviations must always be considered.

Another area that will require attention in a full-scale commercial unit is that some problems can be caused by transient process upsets. An adequate explanation of these upsets will usually require extrapolation to steady-state condition. For example, an impurity is present for only 30 minutes in the feed to a reactor with 3 hours residence time, and causes the conversion to drop 2 percent. To determine the seriousness of this feed impurity will require extrapolation to steady-state conditions. The approach to developing a simplified dynamic model is discussed in Chapter 9.

While the “daily monitoring system” has been discussed primarily in process engineering terms, it can also be used for following mechanical equipment. One of the essential areas that can be followed is “mean time between failures”. This is the time that a piece of equipment is in service before it fails. Good records will allow determining whether there is any difference in failure history of a piece of mechanical equipment. In many process plants, there is a strong relationship between the process and mechanical equipment. The problem solver should be careful that he does not exclude events that are occurring in the plant because they are not strictly in his area of training. For example, a decrease in mean time between failures of a mechanical seal may be related to the presence of very small particles in the seal flush fluid. The presence of these particles may be related to some change in process conditions.

The implementation of an effective Daily Monitoring Program can be established using the information discussed above along with the following guidelines.

1. Pick 6 to 10 essential variables and graph (computer or hand) them on a *continuous daily basis* using delta graphs and theoretically determined target values. Combine as many variables as is justified based on theory into single graphs. For example, the graph shown in Figure 3-1 combines such variables as catalyst efficiency, reactor residence time, production rate, reactor temperature and reactor pressure into one graph.
2. Establish positive and negative trigger points for each variable. Compare the actual value to the trigger points on a daily basis.
3. Obtain hourly worker comments daily and follow up on any unusual observations.
4. Visually observe equipment in the field at least weekly.
5. Store the essential variable plots so that this information can be easily accessed.

3.3 SOLVING PROBLEMS WITH A DISCIPLINED LEARNED PROBLEM-SOLVING APPROACH

A *Disciplined Learned Problem-Solving Approach* is a technique that allows determining if the problem really occurred and specifying the problem in quantitative terms, as well as resolving the problem accurately and quickly. The approach discussed here *differs significantly* from traditional problem-solving courses. The approach discussed in this book emphasizes using techniques for verifying that the problem really occurred. Many problems presented either are not real problems or are radically different than first described.

In addition, it emphasizes the need to use engineering principles in formulating a hypothesis to explain the problem. In the void problem described earlier, the relationship between voids and production rate is an idea or vision. A scientifically correct hypothesis would be developed by exploring the following logic path along with appropriate calculations. This logic path is as follows:

1. Voids are caused by immiscible volatiles.
2. These volatiles are present due to either or a combination of excessive *immiscible* volatiles in the feed or from a steam leak, poor mass transfer, and/or lack of residence time in the dryer.
3. At this point, additional data could be collected and hypotheses could be developed that explain the data and observations associated with the voids on this specific grade.

The approach in this book also emphasizes that any hypothesis must be confirmed with a plant test or by making “directionally correct changes”. A successful plant test is one that conclusively proves or disproves the hypothesis. The concept of confirming a hypothesis by making “directionally correct changes” will be discussed later. The approach in the book emphasizes that a problem solution must not create new problems.

The *Disciplined Learned Problem-Solving Approach* consists of the following five steps:

Step 1: *Verify that the problem actually occurred.*

Communications in an operating environment are almost always second or third hand and often highly “garbled”. The problem solver must have a means to reduce the confusion at this point.

Step 2: *Write out an accurate statement of what problem you are trying to solve.*

Answers to the following questions may be helpful:

- What happened?
- When did it happen?
- Where did it happen?

- What was the magnitude of the problem?
- What else happened at the same time or shortly before?
- What actions are you planning?

Step 3: ***Develop a theoretically sound working hypothesis that explains as many specifications of the problem as possible.***

Step 4: ***Provide a mechanism to test the hypothesis.***

Step 5: ***Recommend remedial action to eliminate the problem without creating another problem.***

Perhaps the problem verification phase is the most overlooked part of this five-step procedure. The problem of the day often arrives at the problem solver so jumbled that the best approach is to go direct to the “horse’s mouth”. For example, by talking to the operator who is having an equipment-related problem or to the laboratory technician who got a “strange” result, the engineer can find out directly and exactly what was observed. He will often find that the real problem is considerably different than described in an e-mail that he received. Problem verification may also take the form of data verification. While this is the subject of a later discussion, it should be noted here that application of engineering principles can often eliminate a problem by determining the alleged problem was only a defective instrument. For example, an engineer sent to investigate the poor operation of a 40-psig steam desuperheater found that the measured steam temperature was below the temperature of 40 psig saturated steam and yet water did not appear present in the steam. Since this is a theoretically impossible situation, he began to investigate the accuracy of the instrumentation. He determined that the steam temperature instrument had been incorrectly calibrated.

The person directly involved with the problem can usually be helpful in the problem specification phase (Step 2). However, his knowledge base will normally not allow him to formulate technically sound hypotheses although he will normally do so. At this point, it is very important to focus in on the activities of Step 2 (writing an accurate specification of the problem). While this description does not have to be a formal document, *shortcuts or even shorthand to allow getting to the answer quickly will be counterproductive*. The problem statement should be as short as possible while still including pertinent data. There is great value in writing out the problem specification using a structured approach. The structured approach provides a means to uncover gaps in the data. In addition, the writing process forces one to clarify data and thinking.

Table 3-3 shows an example of a problem statement format that could be used. The key part of this format is the problem statement (description of the event). The other parts of this format may or may not be of value depending on the organization needs.

The purpose of this format is to provide a simplified communication tool between the problem solver and different managerial layers, and to

Table 3-3 Problem specification example

SHORT TITLE OF PROBLEM _____

DESCRIPTION OF EVENT (make sure that Step 2 is utilized to provide a complete problem description)

HOW WAS THE PROBLEM DISCOVERED? (Was it by data plotting, operator discussion ...?) _____

PRELIMINARY PROBLEM ASSESSMENT

COST OF PROBLEM (HIGH, MODERATE, LOW) _____

IS IT AN OPERATING OR TECHNICAL PROBLEM? _____

IS THERE AN OBVIOUS IMMEDIATE FIX? _____

IF YES, WHAT IS THE PROBABILITY OF SUCCESS? _____

IF NO, WHAT AMOUNT OF EFFORT IS INVOLVED IN PROVIDING A FIX? _____

ARE YOU ACTIVELY WORKING ON THIS PROBLEM? _____

provide a format to allow the problem solver to both state the problem in problem-solving terms and assess the severity and solution difficulty of the problem.

While this form is only presented to serve as an example, there are two important concepts involved in using this or similar forms. The form should be kept as simple as possible. In addition, the tendency of management to review and edit all documents must be avoided. It should be remembered that this form is only a device to advise management of the status of problem-solving activity in the problem solvers realm of responsibility. Bureaucracy or any type of editing will be counterproductive and will often reduce the desire of the problem solver to use this technique.

The development of a theoretically sound hypothesis (Step 3) to explain the problem is an essential concept to allow industrial problems to be

eliminated. A cause–effect relationship does little good unless the cause can be eliminated or understood. For example, in the “void problem” discussed earlier, reducing the production rate only masks the problem rather than eliminating the problem. An example of a theoretically sound hypothesis for this problem is as follows:

“There is a condensate leak causing water to flow from the steam side of the indirect dryer to the polymer side. This water is trapped in the pores of the polymer flakes. It is not removed when it is heated in the extruder because the extruder does not have a vent. As the particle is cooled, the water condenses forming a second phase in the polymer particle. This second phase is what causes the discontinuity in appearance.”

This hypothesis must be tested against plant data, but it could explain both the appearance of voids and the sensitivity to rate. As the production rates and heat input requirements are increased, the steam pressure on the dryer would have to increase in order to provide the temperature driving force necessary to provide more heat input. This increase in steam pressure would create more leakage potential.

Chapter 5 provides more information on how hypotheses can be formulated. Development of theoretically correct hypotheses will involve the application of engineering principles as described in the following paragraphs.

Unit operations and/or equipment design calculations can be used to formulate hypotheses associated with pump or compressor motor overloading. For example, changes in the pump or compressor horsepower requirements that occur as the composition changes might be used to determine why a motor overloads. Another example could be the calculation of the amount of condensate produced from a steam turbine which then might be used to show that a steam trap was being overloaded resulting in poor performance of a heat exchanger.

Unsteady-state accumulation calculations that allow for analyzing a process in a dynamic mode could be used for determining how fast propane builds up in a polypropylene process. These calculations could also be used to determine how many displacements of a system are required to achieve a given degree of cleanliness during a transition or start-up operation.

Mass and Energy balances can be used for analyzing steady-state or dynamic operations. Examples of the use of these balances for dynamic operations are how hot would the wall of a reactor become if heat transfer failed? Or how long could a process operate without cooling water?

The development of a theoretically correct working hypothesis is mandatory to reduce the unlimited number of hypotheses to a few that make sense. *Problem Solving that is not based on theoretically sound hypotheses will degenerate into unstructured brainstorming.* Unstructured brainstorming quickly becomes a contest to determine who can generate the greatest number of hypotheses (sound or unsound).

As the next step (Step 4) is addressed, the definition of a successful plant test must be considered. A successful hypothesis test is often thought of, as one that proves the hypothesis is correct. However, disproving a proposed hypothesis is as valuable as proving one. Therefore, the definition of a successful hypothesis test is a test that either proves or disproves the proposed hypothesis *conclusively*. A failed hypothesis test is simply one that is *inconclusive*. Whether the test proves or disproves the hypothesis, the results of the test must be documented. Even for a test that disproves the hypothesis, documentation is important. This will avoid redoing the test later. This subject is covered in greater detail in Chapter 11.

The mechanism to test the hypothesis can consist of a plant test of new operating conditions, an increased data collection frequency and/or new data, a series of calculations or a temporary “mechanical fix”.

Regardless of which mechanism is selected to test the hypothesis, a great deal of salesmanship will be required to obtain the necessary cooperation from all parties that are involved. The first meeting where the hypothesis test is proposed may be the first encounter with the individual that originally uncovered the problem. Regardless of whether this is true or not, the carefully prepared problem statement and a statement of the theoretically correct working hypothesis will be very beneficial at this point. These two documents, along with the proposed hypothesis test, will provide an outline of the following:

- What problem are you trying to solve?
- What is the working hypothesis?
- How do you plan to prove the hypothesis?

The mode to a successful hypothesis test often lies in the hands of the hourly personnel. If the hypothesis is to be demonstrated by a plant test or by any technique that involves the hourly workforce, the need to communicate the goals of the test must not be overlooked. This will also be an opportunity to explain the theoretically correct working hypothesis to the hourly workforce. This pretest communication is an excellent opportunity to teach and train, as well as getting support for the test. A test that fails allegedly because “The operator did not want it to succeed” usually indicates that there was inadequate communication with the operator. The successful problem solver will always have the paradigm that the hourly workforce wants the test to be successful also. Post-test communication is also of value. Such items as the test results, the conclusions and future plans will help ensure future positive results.

While a plant test is a typical approach to testing a hypothesis, increased data collection can also be used as a test mode. While this appears to be an obvious statement, the presence of highly specialized techniques for obtaining additional data should be considered. Examples are as follows:

- Temperature measurements using infrared detectors can be used to either supplement and/or confirm existing instrumentation.
- High-speed data acquisition devices can often be of benefit to determine the exact sequence of events.
- A specially designed venturi flowmeter can be used to detect the presence of two-way flow in a pipe.
- X-ray pictures of equipment can be used to confirm the presence of a plugged downcomer or a damaged fractionation tray.
- Qualitative laboratory tests can be used to confirm the presence of an element that could only be present if an “O-ring” were failing.

The important consideration is to use all the resources available and “think outside the box” to allow the proposed hypothesis to be *conclusively* tested.

While it is similar to a plant test, a temporary mechanical fix can be used to provide a test of a hypothesis. This approach provides a circuitous route to proving/disproving a hypothesis. In cases where a plant test is undesirable or would require an excessive amount of time, a temporary mechanical fix may allow confirming the hypothesis. The problem solver will use logic prior to the mechanical fix to specify what criteria would be required to demonstrate that the hypothesis was correct. The logic might be stated as “If the hypothesis is true and the proposed mechanical fix is made, the following will be observed _____.” If the anticipated results are obtained, the hypothesis is confirmed with some degree of certainty. However, there is always the possibility that the hypothesis was wrong and the mechanical fix, while providing the anticipated results, did so because of a different hypothesis than proposed. A specific example of this approach is discussed in Chapter 4.

Once a proposed hypothesis has been demonstrated to be true, the problem must now be *eradicated* (Step 5). The three keys to Step 5 (*Recommend* remedial action to *eliminate* the problem without creating another problem) are as follows:

1. In order to avoid creating another problem with the solution to the initial problem, a thorough potential problem analysis should be conducted. A potential problem analysis is a technique for visualizing what problems might occur if the recommended solution is implemented. Once a potential problem is discovered, consideration can be given to eliminating or ameliorating the problem via preventative or contingency actions. *This analysis should include safety aspects also.*
2. Make sure that the problem solution is the simplest one that will work. Keeping things simple is even more important in problem solving than in plant design. Make sure that in attempting to provide a perfect solution, that the solution complexity does not create a trap.
3. Make allowances for “follow-up”. New operating or maintenance techniques will require a great deal of “nagging”, “hand-holding” and “coddling” to keep them from being forgotten or ignored.

3.4 DETERMINING THE OPTIMUM TECHNICAL DEPTH

Any discussion of optimum technical depth is meant to apply to those process problems that require serious engineering considerations. There are large numbers of process plant problems that are best solved by intuitive judgment and experience-based know-how as discussed in Chapter 1. Some of these manifest themselves in emergency and start-up situations. In those situations, there is no question of *optimum technical depth*. Things must be done quickly with little time for introspective analysis.

However, for those problems that require engineering analysis, there will always be a question of the required technical depth. For the purpose of this discussion, *optimum technical depth* can be defined as “the ability to compromise between expediency and thoroughness in order to solve a process problem in a minimum amount of time”. This definition is shown schematically in Figure 3-2.

This is an exceptionally difficult area to quantify. It will vary greatly from company to company. Even in the same company different divisions appear to have different standards. A few definitions are required before proceeding further.

Confidence level is defined as the probability that the recommended problem solution will completely eliminate the problem without creating another problem. There are two different confidence levels to be considered. One is the required confidence level as suggested by management. The other is the probable confidence level as assessed by the problem solver. In order to avoid misunderstandings, the probable confidence level should be greater than the required confidence level.

Project execution time is the amount of time required from the time that the problem solver begins to work on the problem until the problem is solved. This involves time for data collection, data analysis and implementation of operating changes or installation of mechanical equipment. Obviously this can be as short as a few days to as long as several months.

In spite of the difficulty in quantifying optimum technical depth, the problem solver should give consideration to this variable prior to initiating problem-

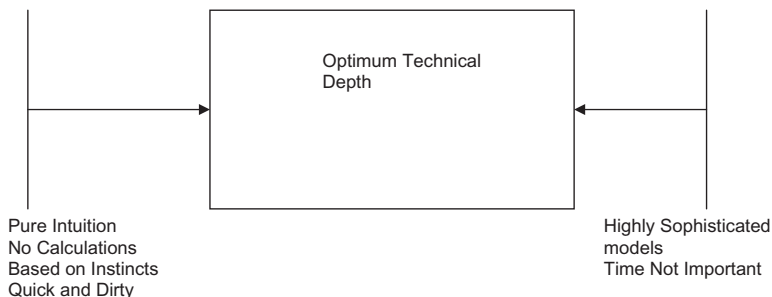


Figure 3-2 Optimum technical depth schematic.

solving efforts. Some suggested guidelines that may help in quantifying the optimum technical depth are provided in the following paragraphs.

The *probable* confidence level that the problem solution is correct is directly proportional to the technical depth involved in the problem-solving activity. For example, a pressure drop calculation that assumes the length of the line is about 200 feet is much less accurate than a calculation based on line measurement and a count of the number of fittings.

The *required* confidence level in an industrial environment is much lower than in an academic or research environment. The courtrooms are filled with examples from the pharmaceutical and medical research fields of alleged inadequate required confidence levels. In an industrial environment, where product liability is not an issue, the daily cost of the process problem often dictates the need for a lower required confidence level. The exception to this is where safety or product liability is involved. In these cases, there is a need to have a high degree of confidence that the urgency to solve a process problem does not create a product liability or safety-related problem.

The *required* confidence level is directly proportional to the cost of the solution and/or the execution time of the solution. Often the solution to a process problem involves the engineering and construction of additional facilities. This can require a period of 12 to 48 months depending on the complexity of the design. These facilities can often be very costly. If the chosen problem solution will require additional facilities, the problem solver should have a great deal of confidence that the revisions will result in a true problem solution. On the other hand, there are problem solutions that require minimal cost and can be installed quickly. These will require a lower degree of confidence prior to installation.

The *required* confidence level is also directly proportional to the cost of the problem. That is, the required confidence levels for solutions to costly problems are higher than those for the less costly problems. In an industrial environment, the costly problems also get the greatest visibility. That is, they get more management attention and as such require a higher degree of confidence in the problem solution. The less costly problems that require a long execution time or involve a large expense for equipment also require a high confidence level in the chosen solution. The less costly problems that can be solved by a quick low-cost fix do not require as high a confidence level.

Unfortunately, the very expensive problems often require a detailed technical analysis. Since they are expensive, they create a lot of pressure to develop a quick fix. Rather than doing the required technical analysis, the problem solver often submits to the temptation to “try something”. He then finds himself spending some of his limited amount of time implementing the “something” multiple times rather than doing a detailed technical analysis.

Another aspect of assessing the optimum technical depth involves estimating the project execution time. For typical engineering projects, most industrial companies have well-established project execution times. However for problem solving, these engineering and construction guidelines will likely not

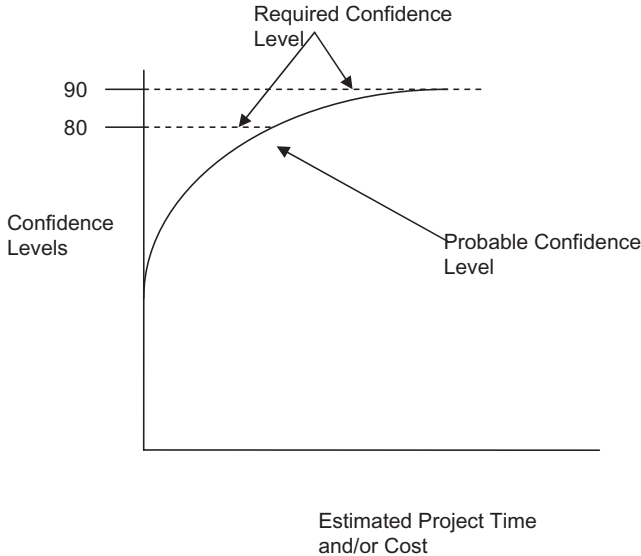


Figure 3-3 Probable and required confidence levels.

be applicable. The problem solver is the best-equipped person to make an estimate of the work that needs to be done and the amount of time and resources that will be required. Once the number of man-days for completion of the project is known, the manning can be estimated. As a very general rule, if the estimated project execution time exceeds 3 months, it will be desirable to increase the manning so that the execution time can be reduced to 3 months or less.

There is always a minimum degree of confidence that is acceptable regardless of the cost of the problem, cost of project execution or length of project execution. It would seem that one should be at least 70 percent confident of the problem solution before it is proposed.

These concepts are illustrated in Figure 3-3. In this figure, the required and probable confidence levels are shown on the y-axis. The x-axis is the project execution time and/or project cost. Thus, as the project execution time and/or the project cost increase, the probability of success also increases. Two levels of required confidence are shown (80 and 90 percent). The required confidence level is set by discussions at the start of the project. It should be realized that these discussions may well start off with some generalized statements such as “Just get it right” or “Do something quick”. These can be translated into required confidence levels that provide some idea of what degree of certainty is required before a recommendation is presented. Obviously these are very subjective evaluations. However, the time that it takes to do them will eliminate future disappointment when recommendations are presented. This effort will also allow the problem solver to indicate to manage-

ment whether the project can be accomplished with the required confidence level in the time and cost constraints that have been determined.

As indicated earlier, the goal of any problem-solving exercise is to obtain a true solution to the process problem in the minimum amount of time. It may be possible to do this by either:

- A detailed analysis that leads to one unique solution with a high probable confidence level that exceeds the required confidence level.
- A multitude of attempts to solve the problem. Each of these attempts will likely have a probable confidence level less than the required confidence level. However, because each of these attempts is done sequentially, the problem will eventually be solved. It should be noted that this concept still requires a technical analysis to confirm that each attempt to solve the problem is a theoretically correct hypothesis. The technical analysis is not a detailed analysis and therefore each attempted solution has a low probable confidence level.

It is possible that the problem solver will have to consider both of these execution approaches. Management may indicate that the required resources are not available or that the required execution time is too long for the alternative with a high probable confidence level (detailed analysis). In this situation, the problem solver can help make an execution plan decision by providing management with his best assessment of the alternative execution strategy. One way of doing this is shown in Figure 3-4. The hypothetical example shown in this figure presents two approaches to solving the same problem. In this example, there is one unique solution to the problem. In one approach, this solution can be reached with a 90 percent probable confidence level with detailed study. The *x*-axis is the cost and/or the length of time required to

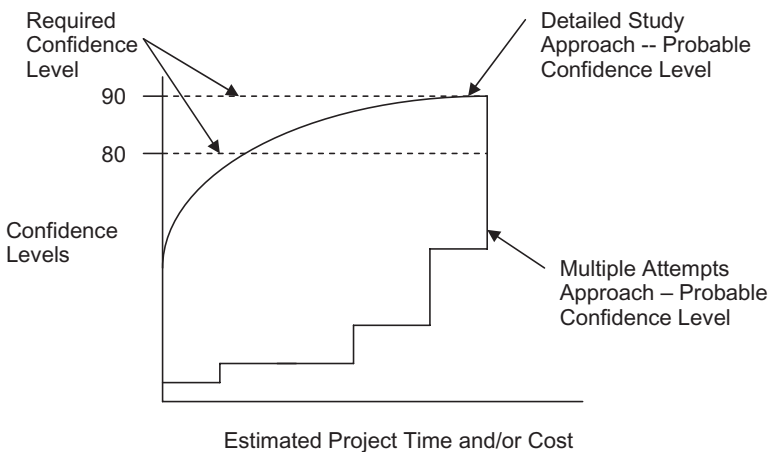


Figure 3.4 Detailed study approach compared to multiple attempts approach.

reach this solution. The y -axis represents the probable and required confidence levels. In the first approach (detailed study), the required confidence level is reached by a single path. The more detailed the study is, the higher is the probability of success. In the alternative approach that uses multiple attempts to solve the problem, the required confidence level is reached, but only after several failed attempts.

In this example, the times/costs have been adjusted so that the 90 percent confidence level is reached after the same expenditure of cost and/or time for both approaches. This is not the normal chain of events. Normally, the detailed study will allow reaching the required confidence level in less time and at a lower cost. Figure 3-4 also shows what happens in the hypothetical example if the required confidence level is reduced to 80 percent. In this case, the detailed analysis will allow reaching this level faster and/or at a lower cost. This is more typical of industrial problem solving. It is realized that this is a highly theoretical example, but it is given to illustrate the thinking that should be done in assessing the best approach to reach a final successful problem solution in a minimum amount of time and/or cost.

Once the solution path can be agreed upon, it can be used to steward the progress of the project using the confidence level versus time/cost type of relationship that was developed to determine the project execution approach. For example in Figure 3-4, if the detailed study route was chosen as the project execution strategy, the problem solver should feel about 85 percent confident in the approach when the project is about 50 percent complete. This is true whether the project is building a mathematical model or installation of new equipment. Progress reports would consist of status of the project, as well as an indication of probability of success. This accountability will allow for any necessary midcourse corrections.

In the second approach of multiple attempts, the relationship can also be used to steward progress. Management reports in this case will likely consist of reports of failed attempts and number of trials remaining. This reporting of multiple failed trials often leads to loss of management confidence in the problem working process.

While it may seem that the above considerations are not worth the effort required, it should be realized that whether this type of thinking is quantified or not, it is going on as any problem-solving exercise is being considered. The proof that such thinking is present is found in statements such as “We have to try something quickly”, “That approach is nice, but it takes too long”, or “Let’s just put in a treatment bed”. When faced with these criticisms, the wise problem solver will attempt to define a cost/timing and confidence level analysis of the various approaches. The above technique is one approach to try to quantify this analysis.

The approach described here can be criticized as attempting to quantify items that are so very subjective that they cannot be quantified. However, it should be realized that whether these items are quantified or not they are always resident in the minds of management and the problem solver. By

attempting to quantify such areas as required confidence level, probable confidence level and execution times, better decisions on approaches and resource allocation will result.

3.5 USING THE DIRECTIONALLY CORRECT HYPOTHESIS APPROACH

There are times that the problem solver will be faced with a problem where he believes that there is a hypothesis that appears to be correct, but because of lack of calculation techniques or lack of technology correlations the hypothesis cannot be proven with calculations. If the problem solver truly has a “directionally correct hypothesis” in mind, this knowledge may by itself lead to an effective problem solution. This approach is different than the trial and error approach where calculations could be made but are not because of the time or cost involved. This “directionally correct hypothesis” approach assumes that if one can make a small and low-cost (in either time or money) change to an independent variable, the impact of this change will by itself either prove or disprove the working hypothesis. The change must be small enough so that no other parts of the process are impacted, but large enough to be confident that the impact if any on the dependent variable is statistically significant. As a general rule, there must be at least a 75 percent confidence level that the independent variable does affect the dependent variable. The sources of these directionally correct hypotheses are likely to be experienced based. The problem solver is likely to have experience with a similar process or similar piece of equipment. In his experience, a problem was solved by a change in an independent variable. He thinks that a similar change will solve the current problem. The hypothesis could be tested by making small and low-cost changes in the process. Since this small change would be expected to make only a small change in the dependent variable, it would be necessary for the process to continue operating in the new mode until sufficient data were accumulated to statistically prove or disprove the theory. It should be noted that this concept still requires a technical analysis and a theoretically correct hypothesis.

An example of this approach is an engineer that has previous experience indicating that there should be a direct correlation between a quality attribute of a product and a plant operating variable. His experience is based on a similar but not identical process. However, in the existing process there is a large amount of scatter in the correlation of the product attribute and the plant operating variable such that there is only a 60 to 70 percent confidence level that there is any correlation at all. Increasing the plant operating variable is the “directionally correct” approach to increase the product attribute. As a test, the plant operating variable can be increased a small amount to determine if there is any change in the product attribute. Over an extended period of time, sufficient data will be collected to show whether or not there is a statistically significant difference in the quality attribute.

A similar approach to this is the need for an efficient means to test hypotheses that have been developed by the detailed analyses methods discussed earlier. It will often be desirable to test hypotheses in a low-cost fashion with minimal disruptions to plant operations. In a case study to be discussed later, two alternative approaches were available to test a hypothesis. One of the approaches would require 215 days at reduced operating conditions to provide a 90 percent confidence level that the hypothesis was correct. The alternative approach required no reduction in operating conditions, could be implemented immediately and was very inexpensive. Thus, it met the criteria of being low cost and having minimal impact on the process. It still required 215 days to provide a 90 percent confidence level that the hypothesis was correct. However, during these 215 days no reduction in operating conditions was required.

EXAMPLES OF PLANT PROBLEM SOLVING

4.1 INDUSTRIAL EXAMPLES

In an industrial environment where the emphasis is usually on increased productivity, doubts about the validity of this technique will always be present. Typical questions are:

- Does this technique really work?
- On what kind of problems can it be used?
- Is it really possible in an industrial environment to use engineering calculations as opposed to intuitive problem solving?

In an attempt to answer these questions, the following examples are presented. The three examples are all actual real-life examples from the polymer industry. Polymers manufacturing problems are often the most difficult to solve and the author's primary experience is in this area. Two of the examples were solved successfully. The first example requires only process engineering skills and the problem solution emphasizes the need for a *daily monitoring system*. The second example requires both minimal knowledge of statistics and mechanical engineering, as well as process engineering skills. The third example is presented to illustrate the problem of inadequate intuitive problem solving.

4.2 POLYMERIZATION REACTOR EXAMPLE

At 0200 hours on April 2, one of the six continuous polymerization reactors experienced a temperature runaway. That is, the reactor temperature rose exponentially from a normal temperature of 150 to 175°F in a 30-minute period. Polymerization is an exothermic reaction that generates a significant amount of heat for each pound of polymer produced. The heat of reaction is removed by circulating cooling water. Polymerization reaction rates generally double with every 20°F increase in temperature. When the reactor in question reached 175°F, the reaction was terminated by injection of a quench agent. All the other reactors were operating normally.

The temperature control system on the reactor was such that an increase in temperature caused an immediate increase in the cooling water supply flow. It was known that a small increase in catalyst rate occurred right before the temperature began increasing. However in the past, catalyst rate increases of this magnitude only resulted in a slight temperature increase. Following this slight increase, the reactor temperature very quickly returned to normal as the cooling water control system responded. The heat exchanger that is used to remove the heat of polymerization is periodically removed for cleaning. On April 1, the exchanger seemed to be “ok”.

A simplified sketch of the equipment and various data is shown in Figure 4-1.

At this point, the problem solver is faced with at least three questions:

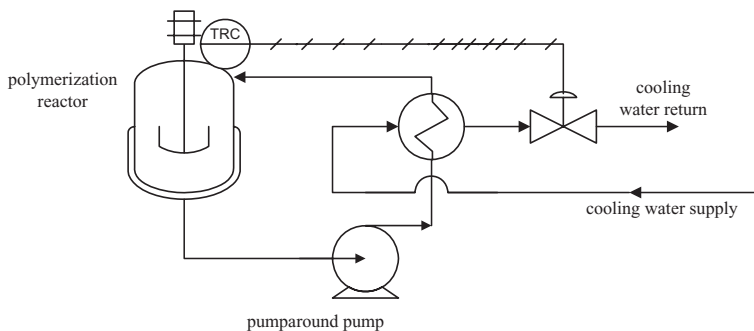
1. What should be done to return the reactor back to service?
2. What caused the episode?
3. What can be done to prevent it from recurring in the future?

The first of these questions can be handled by a combination of good operating practices (clean out the reactor) and intuitive problem solving (the exchanger should be cleaned). However, the last two can best be approached by the problem-solving techniques discussed in the previous chapters.

4.3 APPLICATION OF THE DISCIPLINED PROBLEM-SOLVING APPROACH

Step 1: *Verify that the Problem Actually Occurred*

While on first glance there may not seem to be a need to do this step, the problem solver made a cursory review of all variables to confirm that the reaction really was terminated due to a “temperature runaway”. He found that all temperature instruments indicated an increase in temperature. In addition, the pressure on the reactor also increased.



Data Values at Midnight

Temperatures

Cooling Water	
In	90
Out	120
Pumparound Liquid	
In	150
Out	142

Flow Rates, pph

Cooling Water	195000
Reactor Slurry Pumparound	2,000,000

Other Information
The valve on the cooling water
is 95 % open

Technology Information

$$\text{Reaction Heat Generated} = K e^{(-11000/T)}$$

Where K is a constant that containing monomer concentration, catalyst concentration, reactor volume and heat of reaction.

$$K = 3.9(10^{14})$$

T is in Rankin

The specific heat of the reaction fluid = 0.5 BTU/lb-F

Figure 4-1 Reactor schematic.

Step 2: Write Out an Accurate Statement of What Problem You Are Trying to Solve

In this example, the problem that should be solved was twofold—what caused the episode? In addition, what can be done to prevent it from recurring in the future? The problem solver developed the following problem statement.

“Temperature control was lost in the polymerization operation on April 2. This loss of control occurred at about 0200 following a very small increase in the reactor temperature caused by a slight increase in catalyst flow. This loss of control occurred on only one of six reactors all operating at the same charge rate on the same feedstock. The reactor had to be removed from service and cleaned prior to restarting polymerization. There was no mechanical or utility failure on

the reactor in question. The weather turned slightly warmer on March 30. Once the reactor temperature began increasing it rose exponentially from 150°F to 175°F in an extended period (30 minutes). Determine what caused this loss of control, and once the cause has been determined, develop recommendations to prevent this problem from recurring.”

Step 3: Develop a *Theoretically Sound Working Hypothesis* that Explains the Problem

Several possible hypotheses could be proposed and the problem statement could eliminate all but one as shown in Table 4-1.

Thus, a theoretically sound working hypothesis developed by the problem solver was:

“The temperature runaway was caused by the fact that the rate that heat generation increased with temperature was greater than the rate that heat removal increased with temperature.”

Or mathematically:

$$dQ_g/dT > dQ_r/dT \tag{4-1}$$

Where:

dQ_g/dT = the rate that heat generation increases with temperature
 dQ_r/dT = the rate that heat removal increases with temperature

This working hypothesis would predict a loss of temperature control. In addition, since the rate of reaction increased with temperature this hypothesis would also predict an exponential increase in temperature.

Step 4: Provide a Mechanism to Test the Hypothesis

While testing a hypothesis often involves experimental work, using fundamentally correct engineering calculations can also test hypotheses. In this case, experimental work would involve the risk of another loss of reactor

Table 4-1 Hypotheses conclusions

Hypothesis	Why It Can Be Eliminated
Recirculation pump stopped	“No mechanical failure”
Pumparound exchanger plugged	“No mechanical failure”
Cooling water supply lost	“No utility failure”
Catalyst activated by feedstock	“Only occurred on one reactor”
Heat generated > heat removal capability	Not eliminated

temperature control. Thus, the problem solver used engineering calculations as the best approach to testing the hypothesis. These calculations are shown below:

Hypothesis

$$dQ_g/dT > dQ_r/dT \quad (4-1)$$

Engineering calculations

$$Q_g = K * e^{(-11000/T)} \quad (4-2)$$

Equation (4-2) is a typical Arrhenius equation for polymerization. Note that the Gas Constant, R, has been incorporated into the numerical exponent constant.

In equation (4-2):

K = a constant that depends on monomer and catalyst concentrations, reactor volume, and heat of polymerization. A typical value for this specific process and operating conditions is $3.9(10^{14})$

T = absolute temperature, °R

Equation (4-2) can be differentiated with respect to the absolute temperature, T, to give the rate that heat generated increases with respect to temperature as shown in equation (4-3).

$$dQ_g/dT = (K * 11000 / T^2) * e^{(-11000/T)} \quad (4-3)$$

The rate that heat is removed from the reactor can be represented by a typical heat removal equation shown in equation (4-4).

$$Q_r = U * A * \ln \Delta T \quad (4-4)$$

Where:

U = the exchanger heat transfer coefficient

A = the exchanger surface area

$\ln \Delta T$ = the log temperature difference between the polymerization slurry side and the cooling water side

Since as noted in Figure 4-1, the cooling water flow is almost at a maximum (valve is 95 percent open), the average water temperature will not decrease. Therefore, as a first approximation:

$$\ln \Delta T = (T - T_w) \quad (4-5)$$

$$Q_r = U * A * (T - T_w) \quad (4-6)$$

Where:

$(T - T_w)$ = the difference between the average reactor temperature and the average cooling water temperature

In the initial few minutes, the average cooling water temperature will remain constant. Thus, differentiation of equation (4-6) gives equation (4-7).

$$dQ_r/dT = U * A \quad (4-7)$$

By substituting actual values into equation (4-3), equations (4-8) and (4-9) can be developed.

$$dQ_g/dT = 3.9(10^{14}) * (11000 / (610)^2) * (e^{(-11000/610)}) \quad (4-8)$$

$$dQ_g/dT = 170000 \text{ BTU/hr-}^\circ\text{F} \quad (4-9)$$

$U * A$ can be estimated from the midnight values shown in Figure 4-1 using equation (4-10).

$$U * A = Q_r / \ln \Delta T \quad (4-10)$$

Where:

$$Q_r = 5.75(10^6) \text{ BTU/hr}$$

$$\ln \Delta T = 40$$

Therefore,

$$dQ_r/dT = U * A = 144000 \text{ BTU/hr-}^\circ\text{F} \quad (4-11)$$

As indicated earlier, the hypothesis was that—"The temperature runaway was caused by the fact that the rate that heat generation increased with temperature was greater than the rate that heat removal increased with temperature" or mathematically $dQ_g/dT > dQ_r/dT$. Since the calculated value of dQ_g/dT (170000 BTU/hr- $^\circ\text{F}$) exceeds the calculated value of dQ_r/dT (144000 BTU/hr- $^\circ\text{F}$), the hypothesis was proved with calculations.

Step 5: Recommend Remedial Action to Eliminate the Problem without Creating Another Problem

The required remedial action developed by the problem solver consisted of providing operating procedures to insure that the rate of heat removal always

increases faster than the rate of heat generated. Mathematically this can be expressed as follows:

$$dQ_r/dT > dQ_g/dT \quad (4-1)$$

To be conservative, a 10 to 20 percent safety factor should be included. Thus:

$$dQ_r/dT > 1.1 * dQ_g/dT \quad (4-12)$$

From equation (4-9) $dQ_g/dT = 170000 \text{ BTU/hr-}^\circ\text{F}$. Thus:

$$dQ_r/dT > 187000 \text{ BTU/hr-}^\circ\text{F} \quad (4-13)$$

$$\text{or } UA > 187000 \text{ BTU/hr-}^\circ\text{F} \quad (4-14)$$

Therefore to prevent future occurrences, he specified that the exchanger should be removed from service whenever the “UA” drops below 187000 BTU/hr-°F.

Since “UA” could be easily calculated (see equation (4-10)), it became one of the “key variables” that was plotted and monitored on a daily basis. This could be done using the plant process control computer or by hand plotting.

Some may question the need to actually calculate a “UA” value since the narrative indicates that the cooling water was close to a maximum flow rate. While this fact should have been a “red flag” warning to both operations and technical personnel, there is value in being as precise as possible.

It should also be noted that the calculated value of dQ_g/dT depends on both reaction rate and reaction temperature. If the reaction rate increases (larger value of “K”) or the reactor temperature decreases (larger slope of rate versus temperature relationship), the value of dQ_g/dT will increase. This will cause the minimum value of “UA” to increase.

A potential problem analysis might reveal that the main potential problem was the degree of conservativeness used to evaluate the heat removal capacity required. A study of the variability of the rate of reaction would reveal whether the 10 to 20 percent above the dQ_g/dT factor was sufficient. The proposed solution is certainly a simple solution. However, follow-up will be difficult because it will involve requiring that operations remove a “perfectly good” exchanger from service for cleaning to avoid future episodes of temperature runaways.

4.4 LESSONS LEARNED

The value of being as quantitative as possible is actually twofold. The daily monitoring of a numerical value allows for planning of an exchanger downtime

for cleaning as opposed to an “unplanned cleaning” which will always occur at the most inopportune time. If the heat transfer capability were followed on a daily basis in a numerical fashion, the exchanger could be removed from service for cleaning during periods of line downtimes for other mechanical reasons or for downtimes associated with a reduction in sales volumes. In addition, the subjective observation that the cooling water flow was close to a maximum may depend on climatic conditions. These can change rapidly. Thus, what appeared to be a situation where the exchanger had “plenty of capacity” changed quickly as the ambient temperature changed. If the value of the heat transfer coefficient or a comparable value had been calculated, there would be minimal effect of climatic conditions.

Frequently in situations like this, the problem solver that is under time pressures will often just participate in doing whatever is necessary to get the equipment back into service. The question of what should be done to prevent the same or a similar problem from happening in the future is not considered. In this particular case as the problem solver investigated the problem in detail, he uncovered a new area and a new technique that would prevent future temperature runaways.

While the approach that the problem solver used allowed solving the problem and developing a system to prevent future problems, it would have been better to have a more methodical approach to developing a theoretically correct working hypothesis (Step 3). The approach to developing this working hypothesis can be enhanced by a list of questions that will stimulate theoretically correct creative thinking. This list of questions will be given in Chapter 5.

4.5 MULTIPLE ENGINEERING DISCIPLINES EXAMPLE

This example illustrates the value of a disciplined problem-solving approach when dealing with people or organizations that appear to have fixed positions based on sound logic, but inadequate data. In addition, it also illustrates the advantages for making simple changes to test hypotheses.

A process plant using a rotary filter shown in Figure 4-2 was plagued by excessive downtimes caused by tears of the screen cloth. The fine mesh screen cloth covered the rotating metal drum. It was held in place against the metal drum by retainers. These excessive downtimes occurred on only one out of three rotary filters. These filters were thought to be operating under essentially the same conditions.

Whenever the screen cloth would tear, solids would enter the liquid stream causing a shutdown of critical equipment and a resulting shutdown of the plant. After each screen cloth tear, the screen cloth and rotating metal filter drum were carefully examined. The examinations showed that the metal drum would be scratched. There was not any apparent reason for the scratches. That is, there was no residual that could have caused the scratches. Solids would

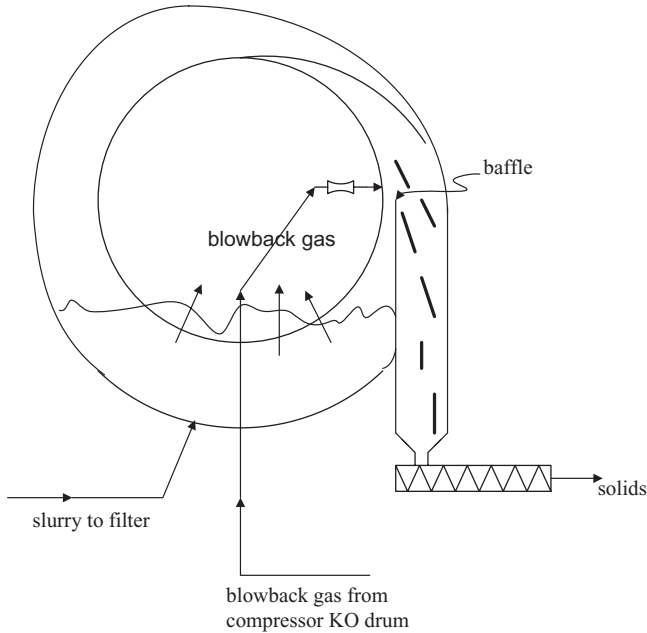


Figure 4-2 Rotary filter schematic.

be present between the cloth and the drum. This was not surprising since the cloth was torn and it was known that solids had passed into the filtrate. The cloth would be torn in a circumferential manner with most of the tears and drum scratches occurring in the middle 60 to 70 percent of the rotating drum.

Even after this careful observation of the filter, no consensus conclusions were reached concerning the failure. In fact, several heated arguments developed with several fixed positions being taken. The mechanical engineers believed that the hard solid polymer particles were cutting the cloth. They believed that these polymer particles were so small that they leaked through the cloth and around the cloth retaining facilities. The process engineer believed that some hard metallic part of the filter was rubbing against the cloth and the metal drum. This would cause the cutting and failure of the screen cloth letting large amounts of solids into the filtrate, as well as scratching the metal drum. He thought that the baffle, which isolated the solids from the filtrate, might be the part of the filter that was rubbing against the cloth and drum. However, he had no explanation for how this might happen since there was acceptable clearance between the baffle and rotating drum.

Since there were people in the research organization that were experienced in this process, they were also called for assistance. They believed that there was liquid in the blowback gas and that this liquid was cutting the cloth. This would allow solids to enter the filtrate and also to scratch the rotating metal drum.

Faced with such a diversity of opinions and minimal data, the problem solver approached the problem using the five-step approach discussed earlier. He made a decision to obtain as much data as possible from all sources.

**4.6 APPLICATION OF DISCIPLINED
PROBLEM-SOLVING APPROACH**

Step 1: Verify that the Problem Actually Occurred

In this example, there was no doubt that the problem actually occurred. However, there was considerable question whether the problem was worse than in previous years. That is, problem verification consisted of considering if there has been a change in the frequency of screen cloth tears.

A review of mechanical records indicated the following as shown in Table 4-2.

Obviously, a problem existed. It should be noted that without detailed mechanical records (daily monitoring), quantifying the extent of the problem would have been impossible.

A further review of what changed between the past and current data revealed that the filtration temperature on this filter was increased from 130 to 170°F. There was a significant advantage to operating at the higher filtration temperature so that returning to the previous process conditions was not a satisfactory solution to the problem.

Step 2: Write Out an *Accurate* Statement of What Problem You Are Trying to *Solve*

The following problem statement was written by the problem solver:

“There has been a significant increase in screen tearing frequency that occurred on only one filter of three filters. This increase appeared to occur at the same time as the filtration temperature was raised. In addition, to a reduction in mean time between screen failures (increased frequency), the nature of the screen failure changed. Previous failures were fatigue failure caused by the cloth being

Table 4-2 Mechanical history

Time Period	Mean Time Between Failures, Days	Type of Tear
Past data	43	Horizontal along the tension rods that held cloth in place
Current data (all runs)	16	Circumferential
Current data excluding the very short runs	25	Circumferential

weakened during flexing while being held in place by the tension rods. The current failure is a catastrophic circumferential failure. The current failure is also characterized by scratch marks on the metal drum. Determine the cause for the significant change in screen tearing frequency. In addition, recommendations should be made for what changes are necessary to eliminate this problem.”

Step 3: Develop a *Theoretically Sound Working Hypothesis* that Explains the Problem

Since the new failure mode appears to be related to the increase in filtration temperature, the following three hypotheses were developed:

1. The screen cloth is decomposing at the higher temperatures.
2. The baffle (see Figure 4-2) is expanding due to thermal growth and bowing into the filter cloth and metal drum.
3. The rotating drum is deforming at the higher temperatures causing poor distribution of blowback gas. The poor distribution causes an increase in blowback gas in the middle of the drum that then blows the filter cloth into the baffle causing the cloth to tear.

Of these hypotheses, only the single hypothesis of baffle expansion could account for *both* screen cloth tears and scratches on the metal drum. The baffle position required to cause the observed failures is shown in Figure 4-3.

Step 4: Provide a Mechanism to Test the Hypothesis

This hypothesis was tested by calculations of thermal growth of the baffle as shown below:

Given:

Original baffle length = 50 inches

Original distance between baffle and rotary drum = 1/2 inch

Coefficient of linear expansion = 0.000011 inch/inch-°F

A typical relationship relating length to temperature is as follows:

$$l_t - l_o = l_o * .000011 * dt \quad (4-15)$$

Where:

l_t = the baffle length at the new temperature

l_o = the original baffle length

dt = the change in temperature, °F

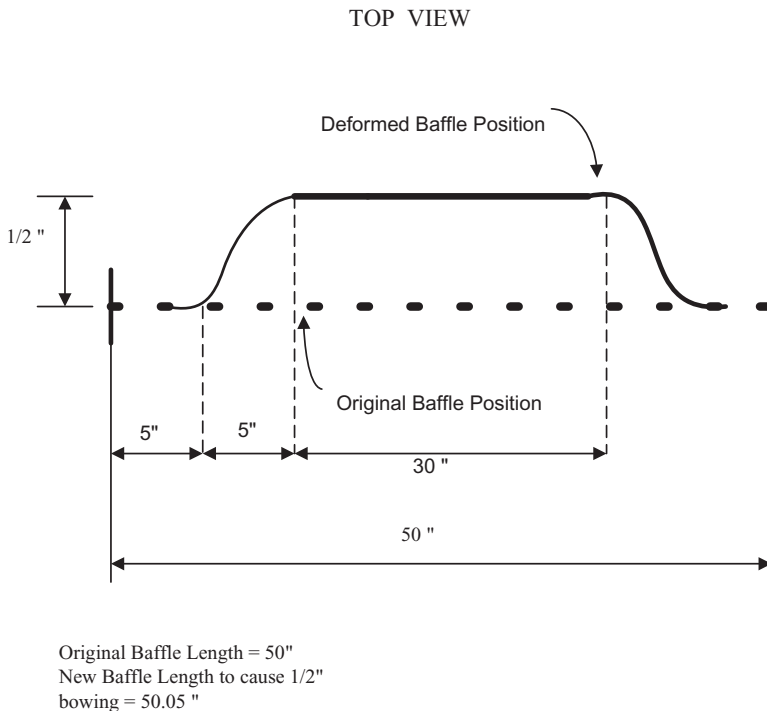


Figure 4-3 Hypothetical baffle deformation.

Considering the baffle shape shown in Figure 4-3, the baffle would only have to grow 0.05" to cause it to bow into the rotating drum. Thus, the new baffle length would be 50.05". The increase in temperature that would cause this amount of growth was calculated using equation (4-15) as shown below in equation (4-16).

$$dt = 0.05 / (50 * .000011) = 90^{\circ}\text{F} \quad (4-16)$$

As these calculations indicated, the baffle would be expected to grow sufficiently to expand into the metal drum and screen if the differences between the filtration temperature and ambient temperature exceeded 90°F. Thus, an increase in filtration temperature from 130 to 170°F significantly increased the probability of the baffle bowing into the drum. The fact that the baffle could also bow away from the drum without any particular consequences explained why failures did not always occur when the temperature difference approached 90°F.

Two alternatives were available for further testing this hypothesis. The filtration temperature could be reduced back to the level of previous operations. A second possibility was that a mechanical constraint could be provided to cause the baffle to always bow away from the drum.

Table 4-3 Statistical data

Period	Mean Time Between Failures, Days	Runs
Before hot filtration	43 ± 26	31
After hot filtration	16 ± 10	26

Since hot filtration was desirable for the process, reducing the filtration temperature would only be permissible for testing. In addition, the testing period would have to provide a high degree of confidence that the problem was caused by the higher filtration temperature while involving a minimum amount of time.

An analysis was made to determine the minimum amount of time required to give a 90 percent confidence level that returning to the lower filtration temperature could eliminate the problem. The basic statistical data developed for this analysis are shown in Table 4-3.

In addition, the statistical approach used by the problem solver to determine how to proceed with Step 4 is defined in the following paragraphs.

If the filtration temperature is returned to the lower value, the mean time between failures will increase to the previous value (43 ± 26). It will be assumed that the values of the mean and standard deviation will be the same as “before hot filtration”. The experimental test of returning to the lower filtration temperature needs to be accomplished in the minimum amount of time (minimum number of experimental runs). The large values of the standard deviation (26 and 10) mean that more than a single test run will be required. Thus, the minimum number of runs to prove that there has been a significant statistical improvement from “hot filtration” at the 90 percent confidence level needs to be determined. The minimum number of runs can be determined by using a statistical comparison of the means of hot filtration and of the results after the process is returned to the lower temperature filtration. When statistics are used to compare two values of means, a two-sided test is involved. This comparison of means will produce a numeric value such as “ $A \pm B$ ”. Where “A” is the difference in the means and “B” will depend on the standard deviations and the actual number of runs to be used in the statistical test. To conclude that there is a real difference between hot filtration and cold filtration in the experiment, both possible values of the term “ $A \pm B$ ” must be positive. Since the value of “B” decreases as the number of experimental runs increases, the minimum number of experimental runs will be the number that produces a positive value for both sides of the statistical test. An iterative procedure is required to develop the final answer. The final iteration is shown below:

Assumed number of runs at reduced temperature = 5

$$SE = (s_1^2/n_1 + s_2^2/n_2)^{1/2} = (100/26 + 676/5)^{1/2} = 11.79 \quad (4-17)$$

$$1/\phi = (1/\phi_1) * (s_1^2/n_1 / (s_1^2/n_1 + s_2^2/n_2))^2 + (1/\phi_2) * (s_2^2/n_2 / (s_1^2/n_1 + s_2^2/n_2))^2 \quad (4-18)$$

$$1/\phi = (1/26) * (3.85/139)^2 + (1/5) * (135.2/139)^2 \approx 0.2 \quad (4-19)$$

Where:

SE = standard error for comparing the two means

s = standard deviation of the two samples

n = the number of runs in each sample

ϕ = the degrees of freedom in each sample (number of runs)

From statistical tables for “t” distribution (two-sided at 90 percent confidence level):

$$\mu = 2.01$$

$$\therefore \text{Difference in mean time between failures} = 43 - 16 \pm 2.01 * 11.79 \\ = 3 \text{ to } 50 \text{ days} \quad (4-20)$$

When only four runs at the lower temperature are assumed, the calculated difference in mean time between failures is -1 to 55 . Thus, four runs are not sufficient to provide conclusively significant data. However, when assuming that five runs at the lower temperature, both sides of the statistical test (3 and 50) are positive. This represents the minimum number of runs that are required. At this point the problem solver could say with a 90 percent confidence that returning to the lower temperature filtration would eliminate the high frequency of screen tears. However, it would be difficult to accurately define the anticipated advantage for returning to the lower temperature due to the large standard deviation. More experimental runs would be required to narrow the range of anticipated benefits.

An estimated period of time for these five runs would be $5 * 43$ or 215 days. Thus, after 215 days at the lower temperature filtration (90 percent confidence level), the problem solver could say that returning to the previous temperature conditions will return the average screen cloth life to 43 days. *However*, this does not conclusively prove or disprove the working hypothesis. It only proves or disproves the effect of filtration temperature on the average screen cloth life. There might be another possible hypothesis that explains the problem. In addition, the test does not lead to any acceptable problem solution since it was desirable to operate at hot filtration.

The other alternative testing procedure (adding a mechanical constraint to insure that the baffle always bowed away from the drum) was easy to do and provided a good mechanism to test the “baffle bowing” hypothesis while allowing continued operation at higher filtration temperatures. However, it involved “political risks” since the addition of the mechanical constraint had “never been done this way before”.

Step 5: Recommend Remedial Action to Eliminate the Problem without Creating Another Problem

Selecting the remedial action in this example was a strong function of how the hypothesis was tested. If the process conditions were modified to allow returning to the lower temperature filtration for 215 days, there would be a tendency to recommend staying at the lower temperature operation as a problem solution. Note that since this was undesirable from process considerations, it would not be an acceptable recommendation.

The alternative technique of mechanically constraining the baffle so that it always bowed away from the drum would provide both a testing procedure and a permanent solution. Thus after 215 days, Steps 4 and 5 could both be considered complete. This was the alternative that the problem solver recommended for the test and for the permanent solution. The potential problem analysis focused on how to make sure that sufficient tension was applied to the mechanical constraint to insure that the baffle bowed away from the filter.

4.7 LESSONS LEARNED

As indicated in the problem description, the initial thinking was that all of the filters were operating at essentially the same conditions. Thinking of this kind is almost always present in any problem-solving activity. It is only when one dedicates sufficient time to analyze data that it will almost always be found that the initial reaction of “essentially at the same conditions” or “no process changes were made” is found to be incorrect.

Oftentimes, minor mechanical changes such as adding the baffle brace will provide simple solutions to complex problems. However in this case, a potential problem analysis of the proposed remedial action missed the possibility that the mechanical constraint might fall off the baffle due to corrosion, vibration or metal fatigue. If this happened, the device would likely go with the polymer. This indeed happened and caused failure of downstream equipment and some contamination of the polymer with metal. If this problem had been uncovered in a potential problem analysis, preventative action could have consisted of using a “backup nut” on the constraining device and/or insuring that the bolt and clamp were made out of corrosion-resistant materials. This illustrates the importance of potential problem analyses. Often the problem solver is so intent on moving into the execution phase of a problem solution that he does not give adequate consideration to potential problem analyses. This phase deserves as much attention as developing a problem solution.

Besides the engineering advantage for using the disciplined problem-solving approach in this example, there is also a psychological advantage. Once people take a fixed position on any subject, it is almost impossible to change their mind without sound data. Often it takes more sound data to change a person's

opinion than it would have if the data had been obtained prior to the development of a working hypothesis. Any of the initial positions described by the different engineering disciplines could be *partially* supported with logic. However, it was only after the problem solver uncovered as much data as possible and developed a hypothesis based on this data that a theoretically correct working hypothesis was developed. Normally the application of the proposed approach will significantly narrow the hypotheses down to one or two that can then be tested in Step 4 of the five-step procedure.

4.8 A LOGICAL INTUITIVE APPROACH FAILS

A customer complaint was received at the manufacturing location of a highly regarded supplier of a baled elastomer ($12'' \times 28'' \times 7''$). The customer alleged that he had received some green bales of the product in a recent shipment. The bales were normally a yellow color. The process for manufacturing the elastomer was about 10 years old and a similar problem had never been encountered. When confronted with this complaint, the Operating Department Head used his problem-solving technique and developed the following problem statement:

“The customer complaint has been investigated. We have not made any significant changes in our operation in 10 years except for the use of “magic markers”. Our operators have started carrying “magic markers” to mark equipment that requires maintenance at the next downtime. We believe that one of these markers must have fallen from one of their pockets into the extruder. The subsequent fracture and dispersion of the material caused several bales to have a green appearance.”

This intuitive logical approach overlooked several areas that a more structured procedure would have uncovered. There was no verification that the problem really occurred. It would have been valuable for the customer to send a sample of the material that he received. The problem definition was incomplete. Consideration of other questions such as the following would have been helpful in a better problem statement.

- What shift did the problem occur on?
- Did other customers notice the problem?
- How many bales were green?
- Did the problem occur on all lines?
- Did laboratory retain samples on the problem date, previous dates or subsequent dates show green color?
- Were there really no operational changes?
- Were the bales green when they were boxed?

In addition to problem definition failures, the hypothesis was not tested against any type of theory. For example, how much of a green magic marker would be required to turn a single yellow bale into a green color? There was no way to estimate the concentration of the green magic marker in the bale since there was no knowledge of the number of green bales. No mechanism was provided to test the hypothesis. The hypothesis could have easily been tested by dropping a green magic marker into the extruder. This would only provide a one-sided test. If the bales did not turn green, the test would be successful in that it would prove that the hypothesis was incorrect. However, if the bales did turn green, it would be necessary to consider the hypothesis in more detail. For example, the following questions should be considered:

- How many bales turned green from a single magic marker?
- Did this correspond to the number of green bales that the customer observed?

Subsequent to the manufacturing manager writing the customer a letter of apology for a magic marker falling into the extruder, several other complaints on the same subject were received from different customers. The continued customer complaints led to the formation of a multidiscipline problem-solving team that determined after a lengthy investigation that the green color was associated with an obscure change in the makeup water used for the polymer-water slurry system.

4.9 LESSONS LEARNED

This example indicates how a failure to adequately develop a problem statement can lead to an embarrassing faulty problem solution. If the problem statement had been fully developed using some of the questions shown above, it is highly likely that the problem would have been recognized as systemic rather than as an individual isolated accident. The failure to adequately define the problem then cascaded to the point that only a simplified logical approach to problem solving was used. If the problem had been recognized as a systemic problem initially, the problem-solving team would have been formed at a much earlier point in time.

This example also illustrates how what appears to be an operation that has not made any changes can be impacted by subtle and obscure changes in utilities. The normal assumption that “water is water” was not true in this case.

Chapter 4 Table of nomenclature

A	The exchanger surface area
dQ_g/dT	The rate that heat generation increases with temperature
dQ_r/dT	The rate that heat removal increases with temperature

dt	The change in temperature, °F
K	A constant that depends on monomer and catalyst concentrations, reactor volume, and heat of polymerization
$\text{Ln}\Delta T$	The log temperature difference between the polymerization slurry side and the cooling water side
l_o	The original baffle length
l_t	The baffle length at the new temperature
n	The number of runs in each sample
s	The standard deviation of the two samples
SE	The standard error for comparing the two means
T	The absolute temperature, R
$(T - T_w)$	The difference between the average reactor temperature and the average cooling water temperature
U	The exchanger heat transfer coefficient
ϕ	The degrees of freedom in each sample (number of runs)

DEVELOPMENT OF WORKING HYPOTHESES

5.1 INTRODUCTION

This book does not deal with the multitude of methods for generating potential working hypotheses. Many of these methods put almost complete emphasis on accurate problem statements. The implicit assumption is that if the problem can be well defined in sufficient detail, that the problem solution will be apparent. In complex process plants, multifaceted problems can rarely be solved with this simple approach.

What is presented in this chapter is an approach for the development of theoretically sound working hypotheses based on consideration of a series of questions. These questions will require an analysis of the data in an introspective fashion. It is highly unlikely that the approach described in this chapter will provide only one possible problem solution. Thus, the chapter and subsequent chapters also deal with how the large number of possible working hypotheses can be narrowed down using logic and most importantly one's technology training.

5.2 AREAS OF TECHNOLOGY

As indicated earlier, there are two kinds of technologies utilized in process plants. These are process-related technologies and equipment-related technologies.

Process technologies are technologies that deal with the specific process. For example, a polymerization process, an isomerization reactor process or a distillation process. The process-specific technologies may include items such as reaction rate kinetics, polymer product attributes or relative volatility data. Each of these processes will have specific technology details that must be well known and understood before attempting to do any process technology-related problem solving.

Equipment-related technologies are technologies that are valid for any specific piece of equipment regardless of the process technology where it is being used. Examples of these are details and calculations associated with pumps, compressors and distillation towers. In addition, most kinetically limited processes (heat transfer for example) can be generalized in terms so that a hypothesis can be developed regardless of the specific technology. This approach to kinetically limited processes is described in detail in Chapter 8.

5.3 FORMULATING HYPOTHESES VIA KEY QUESTIONS

The primary thrust of Chapters 6 through 9 is using the five-step problem-solving procedure discussed in Chapter 3. The equally important parts of having a daily monitoring system and determining the optimum technical depth were adequately covered in Chapters 3 and 4.

The emphasis in this chapter is on formulating and verifying *theoretically sound working hypotheses*. Formulating theoretically sound working hypotheses deals with an in-depth thinking process that requires the problem solver to utilize his engineering training to develop a hypothesis. The in-depth thinking process will rarely be done in meetings. It often requires data analysis, literature research and/or “one on one” discussions with experts in the field or those that can serve as a source of data. This in-depth thinking process often involves consideration of the potential questions shown below to help define the cause of the problem. Examples are given for each question. These examples are not meant to be an inclusive list, but are given only to amplify the specific question. The questions are given in order of priority. Obviously this priority will depend on the specific problem and the specific process. These questions also assume that Steps 1 (Verify that the problem actually occurred) and 2 (*Write out an accurate statement of what problem you are trying to solve*) have been completed.

1. Are all operating directives and procedures being followed?—An inspection of operating conditions at most process plants will show that deviations from procedures and directives are occurring. These may or may not be related to the problem under study. While it is important to verify that all procedures and directives are being followed, a small deviation should not be deemed to be the source of the problem unless

there is a theoretically sound working hypothesis for explaining how the deviation is causing the problem.

2. Are all instruments correct?—Incorrect flowmeters may result in reaction rates being different than expected, fractionation separation being below design levels, a pump or compressor appearing to be operating “off the curve” or failure to adequately strip an impurity from a polymer. A level instrument being wrong could result in reduced or increased reaction rate which would manifest itself as a less than or greater amount of reaction. Heat and material balances are exceptionally good tools and can often be used to answer this question.
3. Are laboratory results correct?—If the problem under study is related in any way to laboratory results, confirming that the laboratory results are correct is a high priority. This confirmation can require review of the procedures as written, review of the procedures as performed and review of the chemicals being used. For example, the results of an extraction procedure can be greatly altered if cyclohexane is used as the solvent when the procedure called for the use of normal hexane.
4. Were there any errors made in the original design?—The high priority given to this possibility is due to the need to assess this question early in the problem-solving activity prior to doing a large amount of work in other areas. This assessment can be made based on experience with the process and the length of time that it has been in operation. The probability that original design errors are causing the operating problem decreases with the age of the process. However, one should not assume that just because a process has been in operation for several months that it is free of design errors. A new operating condition or new product grade may expose design errors that were not detected earlier. These design errors might be as small as a density being wrong on an instrument specification sheet, to as large as incorrect tray selection for a distillation column. The assessment of potential design errors can only be made by either a detailed review of design calculations or redoing the calculations.
5. Were there changes in operating conditions that occurred at the same time as the problem began?—These changes in operating conditions may immediately result in the observation of a process problem. However, the most likely scenario is that everything appears normal when the changes are first made. However at some later point in time, there is a small change in another variable and the problem begins to be noticed. An example of this might be a reduction in the operating temperature of an exothermic reactor in winter. After the reduction in temperature, all control systems appear to be operating normally. However, temperature control was impossible as the outside temperature and hence cooling water temperature increased with spring

conditions. If the process being investigated is integrated with other processes (for example, in a refinery or chemical plant complex), it will be desirable to investigate operating condition changes in these other processes also.

6. Is fluid leakage occurring?—Fluid leakage covers such areas as leakage through heat exchanger tubes, leakage across isolation valves and leakage through control valves. Leakage can cause reaction rates to be less than desired if the leaking component is an impurity. Leakage can also cause an apparent loss of fractionation efficiency or an apparent loss of pumping or compression efficiency. The potential for leakage can be determined by a flow sheet review, determination of pressure flow potential using measured pressures, and in some cases detailed calculations of control valve clearances.
7. Has there been either normal or unusual mechanical wear or changes that could impact performance?—Erosion of wear rings or failure of check valves can greatly affect the performance of pumps and compressors. The performance of distillation columns can suffer due to the failure of a single tray segment. Often the unusual mechanical wear will be caused by a large process upset. Mechanical changes might occur that would affect the process performance. For example, a material of composition change in a mechanical seal might result in decomposition of the seal and contamination of a product.
8. Is the reaction rate as anticipated?—At times reaction rate is the problem that the problem solver is attempting to work. However, there are also times when an excessive amount of reaction or lack of reaction is the cause of a problem itself. For example, alumina desiccant is known to have catalytic properties. The catalytic properties can usually be mitigated by operating techniques. However, if a batch of alumina desiccant has exceptionally high catalytic activity, the normal compensatory operating technique may not be adequate. This may cause problems in the process that can be traced back to the specific batch of alumina.
9. Are there any adverse reactions occurring?—Adverse reactions are always a potential problem with reactive chemicals. The presence of solids in a distillation column that purified a diolefin such as butadiene or isoprene might be traced to small quantities of oxygen that entered the process from inadequately purged storage vessels and then catalyzed the reaction of the diolefin to form a polymer. Another example might be the utilization of aluminum metal in an analyzer sample system when chlorides and olefins were present. The chlorides would react with the aluminum to form aluminum chloride, which would then cause the olefin to polymerize to an oily material and foul the analyzer. The trays in a distillation column might plug due to the presence of solids formed by the unexpected presence of water.

10. Were there errors made in the construction of the process?—Construction errors are treated as a low priority simply because they almost always involve a unit shutdown or elaborate noninvasive techniques to inspect potential problems. However, these errors do occur. Examples of construction errors are debris left in vessels or piping, improper leveling of distillation trays, beveled orifice meters installed backwards, failure to complete the cutting of a “hot tap” so that the flow path is greatly restricted and installation of an incorrect pump impeller.

This list is meant to serve as a possible checklist that can be used to develop hypotheses. It is not meant to be an all-inclusive list. Certainly the priorities will change depending on the specific process and status of the process. However, it is believed that this approach can be effective in developing sound hypotheses.

While the thrust of this book is directed toward equipment-related technologies, the approach to developing working hypotheses can be applied to process technologies as well.

5.4 BEAUTY OF A SIMPLIFIED APPROACH

The problem solver will often be tempted to invent a very complicated theory to explain observations that he does not fully understand. Normally this will be counterproductive. A simple theory will often lead to a problem solution that is easier to execute and more effective. The physicist Ernest Rutherford commented over 100 years ago “A theory that you can’t explain to a bartender is probably no good”.

A real-life example of this concept is found in the history of the building of the Panama Canal. Yellow fever and malaria were serious problems claiming many lives especially during the French period of canal building. Since the worst epidemics seemed to start during the rainy season, the initial theory was that these diseases were caused by mysterious vapors that came out of the swamps which formed during the rainy season. This complex theory provided essentially no readily apparent problem solution. Prior to the American construction of the canal, Dr. Walter Reed and his coworkers in Cuba had developed a simple competing theory to the “swamp theory”. They theorized that yellow fever was spread by the *Stegomyia* mosquito. In addition, they discovered that this mosquito would only lay eggs in clean water held in an artificial container located in or near a building occupied by humans. With this relatively simple theory, problem solutions became readily apparent. This allowed the yellow fever threat in Panama to be greatly mitigated and was one of the keys for successful completion of the Panama Canal. Similar approaches were developed to mitigate the malaria threat.

5.5 VERIFICATION OF PROPOSED HYPOTHESES

In addition to the technique described above, there are multiple alternative problem-solving techniques that are touted throughout the industrial world. All of them involve developing *possible theoretically sound working hypotheses*. These alternative techniques also put emphasis on maximizing the number of possible hypotheses based on the desire to not overlook any possibility. The techniques are of value for generating possible hypotheses. Unfortunately these techniques often result in the assumption that a problem solution that seems logical is also technically correct. This is not always so. The process to verify a proposed working hypothesis is a procedure where the hypothesis is carefully examined using the best available techniques. This verification process can rarely be done without calculations. For example, the hypothesis of an operator that the restriction to the flow of a liquid in a 4-inch line is due to a short section of 2-inch pipe may or may not be technically correct. It can only be assessed as a theoretically sound working hypothesis by calculations. The input of the operator is very valuable since this detail might have been overlooked. However, his conclusion is likely erroneous.

Regardless of how proposed problem hypotheses are developed, they will require verification. It is imperative that the problem solver use his training and calculations to eliminate the hypotheses that are not theoretically correct. These required calculations are part of Step 3 (Develop a *theoretically sound* working hypothesis that explains the problem) or Step 4 (Provide a mechanism to test the hypothesis). Regardless of whether they are included in Step 3 or Step 4, the calculations should be done before proceeding on a plan for a plant test or operating changes.

Many times the problem solver is limited in his problem-solving ability by the lack of proven industrial calculation techniques. For example, pragmatic utilization of pump curves is not taught in the academic world. However, it is exceptionally important in the industry. To aid the problem solver, Chapters 6 through 12 contain hints and useful industrial calculation techniques and approaches. These sections will not be inclusive of all the possible technology and know-how associated with various types of equipment, but are meant to be a summary of valuable techniques and know-how for the process engineer with plant problem-solving responsibilities.

Rather than discussing specific unit operations, the approach in this book is to discuss formulation of the working hypotheses in four areas as follows:

- Prime Movers (pumps and compressors)
- Staged Processes (towers)
- Kinetically Limited Processes (heat transfer, reaction, drying)
- Unsteady-State Processes

It is recognized that most operating companies may have technical manuals that describe how to design particular pieces of equipment. These manuals are usually very voluminous and are aimed at design as opposed to problem

solving. As such the problem solver does not often use them. In Chapters 6 through 9, an attempt is made to reduce the important equipment concepts to those that are required to solve problems. The judgment about what should be included in these concepts is obviously flavored by the author's own experience. An attempt has been made to cover a broad spectrum of process equipment. It is believed that if a specific type of equipment is not mentioned, there will be similar equipment that is described in sufficient detail to allow one to formulate a working hypothesis for the equipment.

5.6 ONE RIOT—ONE RANGER

The Texas Rangers are the oldest law enforcement group with statewide jurisdiction on the North American continent. In the late 1800s according to Texas folklore, there was a small Texas town where a large riot was imminent. The town had limited law enforcement resources. They requested that the governor of Texas send a troop of Texas Rangers to quell the riot. When the train arrived, carrying what the town folks thought would be a troop of Rangers, only one person emerged from the train. When the town folks expressed shock, the Ranger's reply was "One Riot—One Ranger".

While it is true that a committee will always have more knowledge of the facts than any single individual, most effective problem solving is done when one person has the responsibility to solve the problem and uses the input from others. This single individual in process plants is almost always a chemical engineer, process engineer or individual acting in one of these roles. It is extremely important for him to bridge the chasm between his training and others that may have important knowledge or data that will help solve problems. For example, very few chemical engineering curriculums cover mechanical seals. However, mechanical seals are an integral part of a centrifugal pump. Thus when working on a centrifugal pump problem, it is likely that knowledge of mechanical seals will be required. This knowledge can best be obtained by the chemical engineer from discussions with mechanics and/or mechanical engineers.

An example of the need to bridge the chasm between engineering disciplines was a chemical engineer who was asked the question "Is it ok to operate these two identical centrifugal pumps in parallel to obtain increased capacity?" His reply was "I don't know that is an equipment question." In fact, the chemical engineer will be the individual that has the necessary knowledge of process conditions to answer the question. He will have to do a more detailed analysis and develop understanding of centrifugal pumps to finalize the answer to the question. For example, he would have to develop understanding of the following:

- Running pumps in parallel involves determining the exact location on the pump curve (flow rate), determining the capability of the control system to handle the increased pressure drop, and determining the minimum flow that might be encountered during parallel pump operation. These are clearly more than "equipment questions".

- Running pumps in parallel at low flow rates can sometimes result in one of the pumps operating in a “blocked in” condition. If this condition occurs, one of the pumps is pumping the full process flow while the output from the other pump is very little. This “blocked in” operation could create a serious operation and safety problem. This condition could occur, even though the pumps are identical, due to different clearances on the wear rings. This clearly requires consultation between various engineering disciplines.
- Although it is a little known fact, centrifugal pumps often experience a loss of stability similar to what occurs in centrifugal compressors operating at lower flow than the surge point. If a centrifugal pump is operated at flows below this stability point, serious vibration can occur. The chemical engineer would certainly have to depend on another discipline to determine the stability limit.

The primary point of this discussion is that the chemical engineer as a “problem solver” in a process plant must know or obtain knowledge of the equipment that is involved in the problem he is solving. He will often be required to determine why the piece of mechanical equipment does not have as much capacity as it should rather than just saying “It is not operating at design capacity”.

Similar points could be made in the areas of “process chemistry”. A chemical engineer serving as a “problem solver” must obtain the necessary knowledge of the process chemistry to formulate theoretically sound working hypotheses. Once the process chemistry is understood, the same five-step procedure can be used to solve process chemistry-related problems, as well as process equipment problems. The time spent with a chemist familiar with the specific process technology chemistry will greatly aid in formulating correct working hypotheses. This need will be obvious in a process where reactors are utilized. However in almost any process, the possibility for reaction exists. Ignoring the need for completely understanding the process chemistry can lead to formulation of incorrect hypotheses. For example, in a polymer plant, a process engineer developed a hypothesis that the polymer was turning a light shade of pink due to the presence of iron complexes caused by corrosion. A more detailed analysis with a process chemist revealed that one of the additives being used was also a pH indicator and the pink color was due to the slight basicity of the polymer.

In spite of the emphasis on “one ranger one riot” above, the problem solver should never assume or pretend that he has all the knowledge necessary to work the problem. A truly effective problem solver will know and admit his limits. He will then look for help in areas outside of his know-how. However, he will seek this knowledge and apply it to the current problem as opposed to trying to reassign the problem to someone else.

APPLICATION TO PRIME MOVERS

6.1 INTRODUCTION

Prime movers (pumps and compressors) are the workhorses of the process industry. They can be split into two generic categories depending on how they impart energy to the process fluid. These categories are as follows:

- **Kinetic or Dynamic Systems**—Energy is imparted by accelerating the fluid with an impeller and then decelerating the fluid with an inherent rise in pressure. Examples of this type of equipment are centrifugal pumps and compressors, axial and centrifugal fans and blowers. Bernoulli's theory can be used to understand how these prime movers operate.
- **Displacement Systems**—Energy is imparted by displacing the fluid from a lower pressure to a higher pressure with a pushing or rotating action. Examples of this type of equipment are reciprocating pumps and compressors, and rotary blowers and compressors.

In order to formulate theoretically correct working hypotheses for pumps and compressors, knowledge of several relationships and definitions is required. These are summarized in this chapter. In addition, several problems are presented to illustrate the use of these concepts.

6.2 KINETIC SYSTEMS

As indicated above, Bernoulli's theory is the key to understanding these systems. While this theory is usually thought of only in terms of the flow of fluids in piping, it is also valuable when considering the flow of fluids inside a pump or compressor case. Bernoulli's equation is as follows:

$$\Delta P/\rho + \Delta(v^2)/2g_c + \Delta z = -w - lw \quad (6-1)$$

Where:

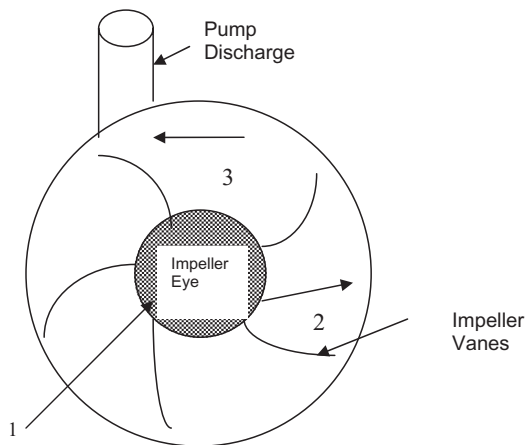
- ΔP = the pressure difference between two points
- ρ = the fluid density
- $\Delta(v^2)$ = the difference in velocity squared between two points
- g_c = the gravitational constant
- Δz = the difference in elevation between two points
- w = the amount of work added by the prime mover
- lw = the frictional loss in the piping system

When considering what happens inside the case of a centrifugal pump or compressor, only the first two terms of equation (6-1) are significant. They clearly indicate that the fluid is accelerated by the work of the prime mover to approach the impeller tip velocity. As the fluid enters the outlet piping, it decelerates and the pressure increases to the discharge pressure. Figure 6-1 shows typical flow path in a centrifugal prime mover.

Bernoulli's theory as applied to centrifugal prime movers has several implications that are of value to consider: The head ($\Delta P/\rho$) that a pump or compressor develops is directly related to impeller tip speed squared. High-speed impellers are required to develop high heads for either pumps or compressors. An alternative is multiple-staged impellers. The high-speed impellers and multiple-staged impellers can also be combined in a single pump or compressor.

The operating characteristic of a centrifugal system (pump or compressor) is defined by the equipment characteristic "head curve". This head curve is developed by the equipment supplier and is provided as part of the equipment purchase. An example is shown in Figure 6-2. In this figure, head and horsepower are shown as a function of flow rate. In addition, the stability limit is also shown. Several generalized points can be made about this figure.

Operation to the left of the stability limit will result in flow instabilities as flow surges forward and then backwards through the prime mover. The stability is usually well defined for compressors and blowers. However for pumps, it is usually 25 to 40 percent of the best efficiency point (BEP). If flow reversal



1. Fluid enters the eye of the impeller by pressure flow from the pump suction flange.
2. It is accelerated by centrifugal force to a velocity approaching the tip velocity of the impeller.
3. As the fluid approaches the discharge, the internals of the pump casing allow it to slow down with the inherent increase in pressure.

Figure 6-1 Flow path in centrifugal equipment.

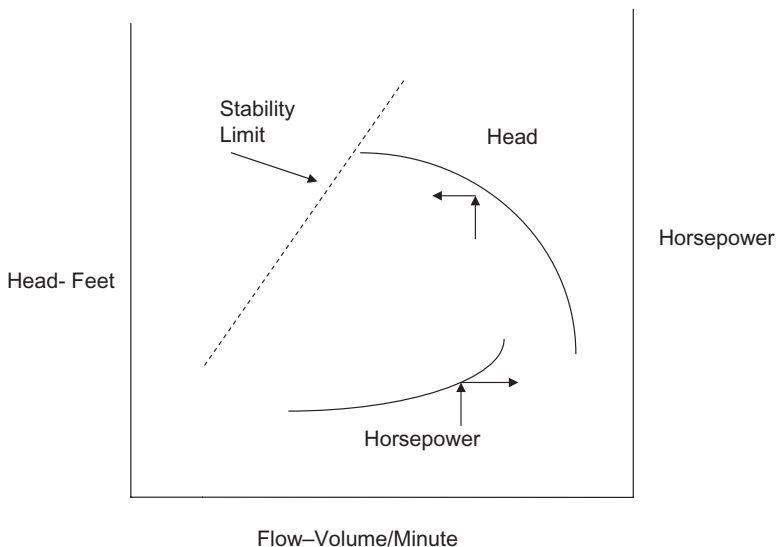


Figure 6-2 Characteristic centrifugal pump or compressor curve.

occurs, it can be damaging to the equipment. Operation of equipment in parallel can sometimes result in operating in the surging region. This happens because the parallel pieces of equipment have different head curves, or often there are slight differences in mechanical characteristics of “identical” pieces of equipment.

The BEP is the point on the “head curve” where the hydraulic efficiency is at a maximum. Note that this efficiency does not include motor efficiency. While the head curve is usually developed using water or air, *it is valid for any fluid if the correct units are utilized for flow and head.* These units are defined later.

As shown in Figure 6-2, the horsepower requirements normally peak at the “end of the curve” (maximum flow rate). The driver for the prime mover may or may not be provided with “end of the curve” protection. If the driver is not designed with “end of the curve” protection in mind, operating at this point will normally cause the driver to be overloaded. If the driver is a steam turbine, it will slow down causing the pump to appear to be operating “off the pump curve”. If the driver is an electric motor, it will shut down as the electrical load causes the motor protection device to react and shut down the motor before the motor fails due to overload.

6.3 PUMP CALCULATIONS

Before considering exact calculation procedures for pumps, a few definitions are required. These definitions are applicable to positive displacement pumps, as well as to centrifugal pumps.

- Cavitation = A condition that occurs if $NPSH_R > NPSH_A$. If this situation occurs, some of the liquid being pumped will vaporize between the pump suction flange and the pump impeller. This will cause the pump to operate off the head curve and damage may occur to the impeller.
- Off the head curve = This is a condition where the actual operating point, as defined by the flow rate in gallons/minute (gpm), and pressure rise, as described by feet of fluid flowing, are below the pump curve as defined in Figure 6-2.
- $NPSH_R$ = Net Positive Head Required. This is the head in feet required to overcome the pressure loss between the pump suction flange and pump impeller eye. The pump supplier will specify this. A typical $NPSH_R$ versus flow rate curve is shown in Figure 6-3. Note that this curve is usually developed with water, but it is valid for any fluid.
- $NPSH_A$ = Net Positive Head Available. This is the difference in feet of head between the actual pressure at the pump suction flange and the vapor pressure of the liquid being pumped. If the liquid has been stored under a nitrogen, air or inert gas blanket, some questions may arise regarding the actual vapor pressure of the liquid. The most conservative

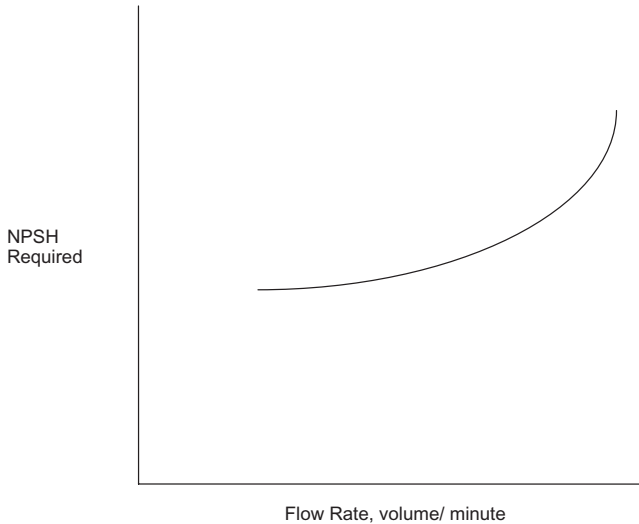


Figure 6-3 Typical NPSH required for centrifugal pump.

approach is to assume that the vapor pressure is equivalent to the pressure in the storage vessel.

The equations below can be used in combination with a pump curve supplied by the manufacturer that is similar to Figure 6-2, to determine essential pump operating characteristics. When using the pump curve for a centrifugal pump, the differential pressure across the pump can be calculated as follows:

$$\Delta P = H * \rho / 144 \quad (6-2)$$

Where:

ΔP = the pressure rise across the pump, psi

H = the pump head at the given flow rate, feet

ρ = the pumped fluid density, lbs/ft³

As indicated earlier, pump curves are usually developed using water as the fluid. They are valid for any fluid as long as the density used for calculations is that of the fluid being pumped. Thus in equation (6-2), the pressure developed by a centrifugal pump can be calculated from the head curve supplied by the pump manufacturer using the head developed at the desired flow rate and the density of the flowing fluid.

The *hydraulic* horsepower for a pump can be estimated as follows:

$$\text{BHP} = H * F * 100 / (E * 33000) \quad (6-3)$$

Where:

BHP = the energy delivered to the fluid, horsepower

F = the flow rate through the pump, lbs/minute

E = the hydraulic pump efficiency, percent

It should be noted that this calculation only includes the hydraulic efficiency. There will be other efficiencies (mechanical and/or electrical) that must also be considered.

On rare occasions, it is necessary to determine the temperature change across the pump. For example, pumps with very low flow rate, high recirculation rate, and high heads may cause significant heat to be generated and conducted to the fluid recycling to the pump suction line. This higher temperature at the pump suction flange may reduce the NPSH_A. The fluid temperature increase across the pump can be estimated as follows:

$$\Delta T = \text{BHP} * (100 - E) * 2545 / (100 * 60 * F * C_p) \quad (6-4)$$

Where:

C_p = the fluid specific heat, BTU/lb-°F

This calculation will often indicate that a cooler is required in the fluid recycle line. Even in high head pumps with low flow and no recirculation, heat generation can be a problem. The heat generated by the pump inefficiency will heat up the fluid, which in turn will reject some of the heat to the pump case.

6.4 CENTRIFUGAL COMPRESSOR CALCULATIONS

As indicated earlier, a head curve similar to that shown in Figure 6-2 is valid for both centrifugal compressors, as well as for pumps. The compressor flow is normally expressed as *actual cubic feet/minute* (ACFM) at the compressor inlet conditions. In addition for a compressor, the calculation of head is much more complicated than for a pump. This is because gases are compressible as opposed to noncompressible liquids. The specific volume for a liquid for all practical purposes can be considered a constant.

While there are multiple references to compression calculations in the literature, two of the references used in the preparation of this book were written by Lyman F. Scheel. They are as follows:

- *Gas Machinery* by Lyman F. Scheel. Published by Gulf Publishing.
- *New Ideas on Centrifugal Compressors Part I* by Lyman F. Scheel. Hydrocarbon Processing, September 1968, Volume 47, Number 9, page 253.

The calculation of head for a compressor depends on the relationship between the pressure and volume of the gas. This relationship is given by the thermodynamic equation:

$$(P \cdot V)^k = \text{constant} \quad (6-5)$$

When applying this relationship to compression (centrifugal or reciprocating), the actual value of “k” depends on which of three thermodynamic assumptions is used. These assumptions are as follows:

1. Isothermal—The constant temperature assumption is impossible to achieve in practice.
2. Adiabatic—This assumption requires that no heat be added or removed from the system. This path can be approached in a piston compressor where the discharge and suction compressor valves have exceptionally large areas. The stipulation of exceptionally large area valves is necessary since the suction and discharge pressures are measured before and after the compressor valves. These compressor valves are flat ribbon valves that are integral to the compressor. However, if the pressures could be measured inside the valves, no stipulation of exceptionally large area suction and discharge valves would be required. In this idealized compression, $k = C_p/C_v$. C_p/C_v is the ratio of the specific heats at constant pressure and constant volume. If compression is adiabatic *and* reversible, it is isentropic compression. That is, it occurs at constant entropy. For this special compression, a Mollier diagram determines the compression path. Like isothermal compression, isentropic compression rarely occurs in practice.
3. Polytropic—This is an empirical assumption for evaluating the compression path in a compressor. However, it is the normal technique to evaluate compression head. For polytropic compression, the “k” value is replaced by “n” which is obtained either from the compressor manufacturer or from plant test data. This will be discussed later.

The polytropic and adiabatic head can be determined from the same basic equation shown below:

$$H = 1545 \cdot T_s \cdot Z \cdot (R^\sigma - 1) / M\sigma \quad (6-6)$$

Where:

H = the polytropic or adiabatic head, feet

T_s = the suction temperature, °R

Z = the average (suction and discharge) compressibility

R = the compression ratio

M = the gas molecular weight

σ = the polytropic or adiabatic compression exponent

There are three different ways to evaluate “ σ ”. They are as follows:

1. The compressor manufacturer may supply the value based on test data.
2. The compressor vendor may supply either the polytropic or adiabatic compression efficiency. In this case, the compression exponent (σ) can be calculated as follows:

$$\sigma = (k - 1) * 100 / (k * E) \quad (6-7)$$

Where:

E = either the adiabatic or polytropic compression efficiency, percent

k = the ratio of specific heats, C_p/C_v

3. The polytropic compression exponent can be calculated from plant data using the following relationship:

$$T_d = T_s * R^\sigma \quad (6-8)$$

Where:

T_d and T_s = the absolute discharge and suction temperatures

It should be recognized that the relationship shown in equation (6-8) gives the compression exponent at any point in time. If the compressor needs mechanical repairs, this value may be higher than predicted by the compressor manufacturer. Since the compression exponent calculated from plant data does vary with mechanical condition of the compressor, this value could be used as a daily monitoring tool for critical compressors. For example, an increase in the compression exponent might indicate that the clearances in a centrifugal compressor had increased to the point that excessive amounts of gas were recirculating to the compressor suction. An increase in the compression exponent for a reciprocating compressor might indicate that the suction and/or discharge valves should be replaced.

Once the head and flow rate are known, the fluid horsepower requirements for the compressor can be easily calculated using equation (6-9):

$$BHP = F * H * 100 / (33000 * E) \quad (6-9)$$

Where:

F = the flow rate, lbs/minute

H = the polytropic or adiabatic head, feet

E = either the adiabatic or polytropic compression efficiency, percent

A word of caution is of value at this point. The compression efficiency (adiabatic or polytropic) should be consistent with the method used for the compression exponent. This will normally be the polytropic efficiency and the polytropic compression exponent. It should also be noted that equation (6-9) includes no mechanical or electrical efficiency that will be associated with belts, gears or motors.

6.5 DISPLACEMENT SYSTEMS

The term “Displacement Systems” refers to the prime movers that displace a fixed amount of fluid (liquid or gas) essentially independent of the differential pressure across the pump or compressor. Typical equipment items that fit this category are reciprocating pumps/compressors and rotary pumps/compressors. While it might be argued that this type of equipment is no longer used in modern plants, an examination of different processes will show that this type of equipment does indeed have a place in a modern process plant. Examples of the use of this type of equipment are as follows:

- Reciprocating compressors where the head requirements are high and the volume rate is low to moderate. An example of this is the high-pressure compression step in low-density polyethylene plants.
- Proportioning pumps with high head requirements or where there is a need to control flow by pump adjustments as opposed to using a flow controller. These might include additive or catalyst pumps.
- Pumps or compressors where it is desired to transfer a fixed rate of material regardless of the discharge pressure. This would not be possible with a typical centrifugal system since the flow rate would decrease as the discharge pressure increased.

There are important concepts in understanding this class of prime movers. It should be realized that with this type of equipment that energy is imparted to the fluid by displacement of a *fixed volume* of that fluid. The mass flow rate will depend on the fluid suction conditions and physical dimensions of the equipment. That is, larger pump or compressor cylinders will allow for displacing a larger volume of fluid, but the mass of fluid moved also depends on the density at *suction conditions*.

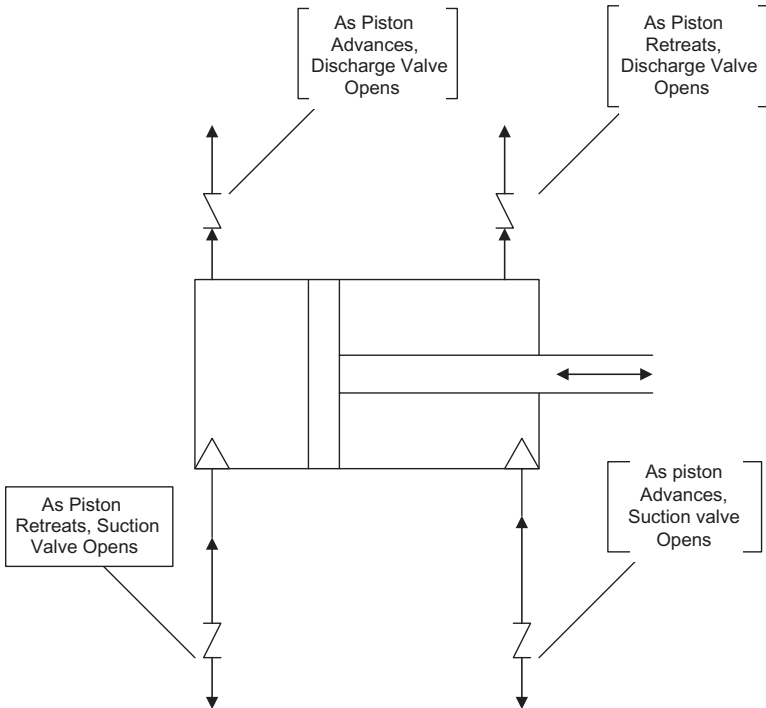


Figure 6-4 Reciprocating flow path in double-acting equipment.

The calculations described in the previous section are applicable to this type of system also. However, head will not be dependent on flow rate. There will be no head versus capacity curve. The pump or compressor head will depend on the suction and discharge pressures only. Figure 6-4 shows a typical flow pattern for a reciprocating pump/compressor.

Some definitions will help in evaluating and understanding this type of equipment. They are as follows:

- **Volumetric Efficiency**—The actual volume of fluid displaced relative to the volume of the cylinder of a reciprocating pump/compressor or rotating pockets of a rotary pump/compressor. For a liquid, this efficiency approaches 100 percent. However for a gas, it is approximately 70 percent. The differences are due to the compressibility of gases. As the pressure in the cylinder or rotating pocket decreases from discharge pressure to suction pressure, the residual gas in the cylinder/pocket expands to partially fill the cylinder/pocket and reduce the volumetric efficiency of the compressor.
- **Leakage**—This is an additional loss in volumetric efficiency caused by leakage through clearances. An example of this leakage in a reciprocating

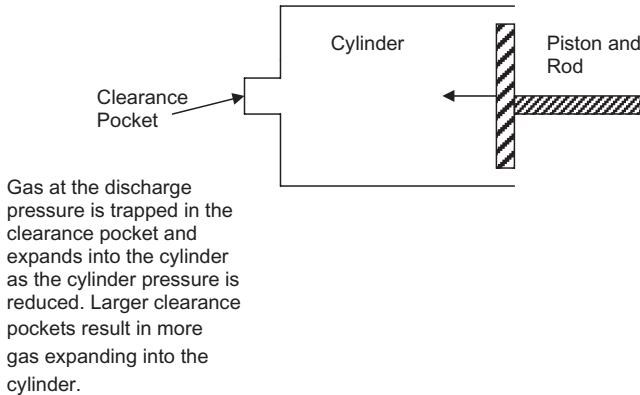


Figure 6-5 Clearance pocket reciprocating compressor.

pump or compressor is the flow of material between the piston and cylinder wall or across the suction and discharge check valves.

- **Horsepower Load Point**—This is a unique feature of a positive displacement compressor. It is the point on a plot of horsepower versus suction pressure where the required fluid horsepower is at a maximum. On one side of this point, increasing the suction pressure increases the mass flow, which overrides the decrease in compression ratio and causes an increase in the required horsepower. On the other side of this point, the increasing suction pressure results in a decreased compression ratio, which more than compensates for the increase in mass flow rate and results in a decreased horsepower. This concept is discussed in more detail later.
- **Clearance**—This is the part of the cylinder in a reciprocating pump/compressor that is not displaced completely by the piston. Figure 6-5 shows a typical sketch of a “clearance pocket”. Because of the compressibility of gases, this becomes more important for gases than for liquids. These are often used to reduce the volumetric efficiency of a compressor and hence the required horsepower.

6.6 DISPLACEMENT PUMP CALCULATIONS

Many of the calculations for displacement pumps are identical to those for centrifugal pumps. For example, equations (6-2) and (6-3) can be used to calculate the head/pressure rise relationship and BHP. The main differences in calculations for the two types of pumps are calculation of the fluid flow rate and $NPSH_A$.

For a single-acting reciprocating pump, the following relationship can be used to estimate the volumetric flow rate.

$$V = \Pi * D^2 * L_s * S * E_v / (4 * 100) \quad (6-10)$$

Where:

- V = the pump capacity, ft³/minute
- D = the diameter of the pump cylinder, feet
- L_s = the length of the pump stroke, feet
- S = the pump speed, rpm
- E_v = the pump volumetric efficiency, percent

There are several points to consider when examining equation (6-10). The pump volumetric capacity is independent of pressure rise and/or pump head except as the discharge pressure decreases the volumetric efficiency. This is different than the relationship between flow and head for a centrifugal pump.

Equation (6-10) is for a single-acting pump. That is, one that displaces the cylinder volume one time for each stroke. The pump that is shown in Figure 6-4 is a double-acting pump. It displaces the cylinder two times for each complete stroke. The capacity of a double-acting pump will be somewhat less than two times that of a single-acting pump of the same dimensions. The actual volume displaced on the return stroke of the piston will be slightly less due to the volume occupied by the piston and piston rod. Equation (6-10) can be modified for more complicated pumps.

The pump design (reciprocating, plunger or rotary) and the mechanical condition of the check valves, and internal pump clearances primarily determine the volumetric efficiency. In addition, for high differential pressure pumps, liquid compressibility must also be considered. If the liquid is compressible, the liquid trapped in the clearances will expand when the pressure decreases from discharge pressure to suction pressure. This will cause the volumetric efficiency to decrease. There will also be more leakage across the check valves with high-pressure pumps.

The determination of the amount of $NPSH_A$ is more complicated for reciprocating-type pumps than for centrifugal or rotary pumps. For any type of pump, pumping a fluid at its boiling point, the $NPSH_A$ is simply the difference in elevation head between the liquid level in the suction drum and the pump suction less the frictional pressure drop. This concept is valid for reciprocating pumps also except the frictional pressure drop must be determined at actual flow rate rather than average flow rate. In addition, since the fluid in the pump suction line must be accelerated from zero velocity to the maximum velocity, there is a pressure loss due to this energy requirement. Fortunately, these two pressure losses occur at different times so that their values are not directly additive. For example, the maximum acceleration head occurs at zero flow rate. Since the flow rate is zero, this is the point of minimum frictional loss. Conversely, the maximum frictional head loss occurs at maximum rate

when there is no acceleration required. For most low-viscosity fluids, the acceleration head dominates. It can be estimated as follows:

1. Calculate the maximum flow rate in the suction pipe.

$$V_p = K * D^2 * L_s * S / (60 * D_p^2) \quad (6-11)$$

Where:

- V_p = the peak velocity in suction pipe, feet/second
- D = the diameter of the pump cylinder, feet
- L_s = the length of the pump stroke, feet
- S = the pump speed, rpm
- D_p = the diameter of the suction pipe, feet
- K = a factor that depends on the pump design

The “K” value for a double-acting pump is approximately $\Pi/2$. “K” values for other style of pumps can be obtained from the pump vendors.

2. Calculate the frictional pressure drop, $(h_F)_{MAX}$, in the suction line using conventional techniques based on the peak velocity calculated using equation (6-11).
3. Calculate the acceleration head required to accelerate the liquid in the suction line from zero velocity to the peak velocity. This can be determined as follows:

$$(h_A)_{MAX} = 1.35 * L_p * S * V_p / 307 \quad (6-12)$$

Where:

- $(h_A)_{MAX}$ = the maximum acceleration head loss, feet
- L_p = the *actual* suction pipe length, feet
- S = the pump speed, rpm
- V_p = the peak velocity in suction pipe from equation (6-11), feet/second

4. The most conservative approach is to determine the suction piping loss by combining the two types of head loss as follows:

$$(h_T)_{MAX} = (h_F)_{MAX}^2 + (h_A)_{MAX}^2 \quad (6-13)$$

Where:

- $(h_T)_{MAX}$ = the maximum suction piping head loss to be used to determine the $NPSH_A$

However, as indicated earlier, these two head losses almost always occur at separate times. Thus, the use of equation (6-13) may give overly conservative predicted head losses. The most reasonable estimate of maximum head loss in the suction piping is the larger of the two losses.

While equation (6-12) appears to be empirical, it can be easily derived from first principles of engineering by realizing that the entire mass in the suction line must be accelerated to the maximum suction line velocity as the suction stroke of the pump begins. The value of 1.35 is an experience-based empirical factor. It is added to allow for the non-sinusoidal motion of the piston and the increased acceleration loss due to elbows and pipe fittings.

Additional information about estimating the $NPSH_A$ for reciprocating pumps can be found in a magazine article entitled "Reciprocating Pumps" by Terry L. Henshaw, *Chemical Engineering*, September 21, 1981, page 105.

Another consideration with displacement pumps is their "on and off" nature. Rather than continuous flow that a centrifugal pump provides, the flow will vary from zero to a maximum rate. In some specialized applications, it may be important to assure that there is always some minimal amount of flow from a displacement type of pump. An example of this might be the need to maintain a continuous flow of catalyst to a polymerization reactor. Stopping the flow of catalyst to the reactor even for a few seconds might result in plugging of the catalyst injection nozzle. Obtaining this continuous flow can be accomplished in a reciprocating pump system by one of two methods. A more complicated duplex or triplex pump can be utilized. These pumps allow for almost continuous flow of the material being pumped. Another alternative is to install a flow surge bottle in the discharge piping of a simplex reciprocating pump. This vessel, which is equipped with an internal bladder and pressured with nitrogen, can be designed so that the discharge flow to the process approaches an average flow rather than a peak flow, followed by a period of zero flow.

6.7 CALCULATIONS FOR POSITIVE DISPLACEMENT COMPRESSORS

As indicated earlier, the head calculations for both types of compressors are identical. Equations (6-6) through (6-9) can be used to evaluate both head and horsepower requirements for a positive displacement compressor. The actual suction and discharge pressure for a reciprocating compressor may be slightly different than measured since the actual pressure is measured in the suction and discharge piping rather than directly at the compressor cylinder during the suction and discharge strokes. In between the compressor cylinder and where the suction and discharge pressures are measured are the ribbon valves. The ribbon valves are pipe diameter size flat devices containing multiple strips of metal. These serve as check valves to isolate the compressor cylinder from

the suction and discharge pressures at the appropriate points in the compressor cycle. For example, when the piston advances causing a buildup of pressure in the cylinder, the suction ribbon valve closes keeping gas from flowing back into the suction piping. If the compressor suction and discharge valves are in good mechanical condition, this pressure difference will not be significant. However, if the valves are partially restricted, the pressure at the compressor will be different than measured. Leakage can also occur in these valves. As indicated earlier, equation (6-8) can be used to monitor the status of these valves for critical compressors.

The flow rate from a positive displacement compressor depends on both the volume of the cylinder or rotating pocket and the volumetric efficiency. As indicated earlier, the volumetric efficiency of a compressor is much lower than that of a pump. This is because gases are very compressible relative to liquids. Volumetric efficiency for a positive displacement compressor can be estimated as follows:

$$E_v = 100 * (1 - L - C * (R^{1/k} - 1)) \quad (6-14)$$

Where:

E_v = the volumetric efficiency, percent

C = the residual gas remaining in the reciprocating compressor clearance pocket or rotating pocket after discharge, fraction of displacement volume

L = the leakage of gas around the piston or rotating element, fraction of displacement volume. It is roughly 2 percent of the compression ratio expressed as a fraction

R = the compression ratio

Horsepower load point is a unique feature of a positive displacement compressor. As shown in Figure 6-6, it is the suction pressure at which the BHP reaches a maximum.

To the right of the horsepower load point, the compression ratio and head are decreasing, but the mass flow is increasing. To the left of the load point, the compression ratio and head are increasing while the mass flow is decreasing. Thus for a positive displacement compressor, driver overload can occur when the suction pressure is either rising or falling. A single-stage reciprocating compressor, with a constant discharge pressure, constant volumetric efficiency and an approximate clearance pocket volume of 10 percent, will reach a maximum horsepower loading at an approximate compression ratio of:

$$R = 1.1 * (n + 1) \quad (6-15)$$

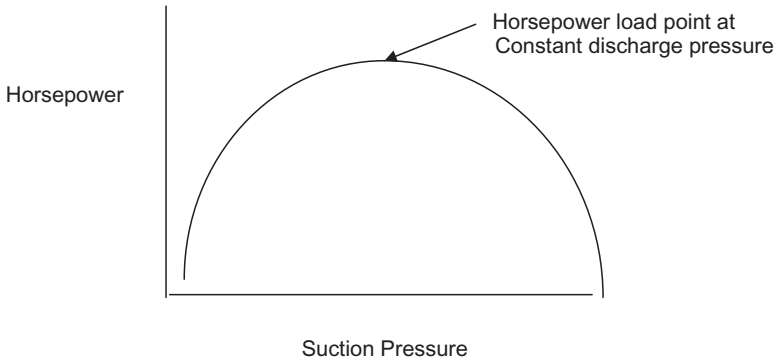


Figure 6-6 Positive displacement compressor load point.

Where:

R = the compression ratio

n = the constant used to define the polytropic compression exponent $\sigma = (n - 1)/n$

Multiple-stage compressors are more complicated, but the concept that decreasing the compression ratio does not always decrease the horsepower requirements is still valid.

6.8 PROBLEM-SOLVING CONSIDERATIONS FOR BOTH SYSTEMS

Compressors

For critical compressors, the suction and discharge temperatures should be used to monitor compressor performance. As indicated previously, equation (6-8) can be used on a daily basis to monitor the performance of a critical centrifugal or positive displacement compressor. If the compression exponent (α) begins to increase, it is an indication that the compressor is becoming less efficient. Another approach that uses the same inputs is to calculate the “leakage” from the discharge pressure to the suction pressure. An increase in this leakage occurs due to mechanical wear caused by increased clearances in the compressor. This leakage can be calculated as follows:

$$L = ((T_D / (P_D / P_S)^\sigma) - T_S) / (T_D + \Delta T_H - T_S) \quad (6-16)$$

Where:

L = the discharge to suction leakage, fraction of volumetric flow

T_D = the discharge temperature, °R

- T_s = the suction temperature, °R
 ΔT_H = the Joule Thompson cooling effect, °R
 P_D = the discharge pressure, psia
 P_s = the suction pressure, psia
 σ = the compression exponent

The Joule Thompson cooling effect is the amount of temperature change that would be expected as the pressure is lowered from discharge pressure to suction pressure.

A similar approach can be utilized for monitoring steam turbines that are often used as drivers on large pumps and compressors. The efficiency of a steam turbine can be determined by comparing the actual change in enthalpy with that predicted assuming an isentropic (constant entropy) expansion. That is:

$$E_T = 100 * (H_I - H_O) / (H_I - H_E) \quad (6-17)$$

Where:

- E_T = the turbine efficiency, percent
 H_I = the inlet steam enthalpy, BTU/lb
 H_O = the outlet steam enthalpy, BTU/lb
 H_E = the outlet steam enthalpy with isentropic expansion, BTU/lb

For critical turbines, the efficiency can be calculated and monitored on a daily basis. This will allow spotting mechanical problems before they become so severe that an immediate repair is required.

For centrifugal compressors, the compressor performance curve supplied by the compressor manufacturer can be used to analyze problems. To do this accurately will require careful planning and consideration. The following items should be included in any planned problem-solving activity associated with compressors:

- Make sure that all field instruments have been calibrated before taking any data.
- Determine the kinetic head as described in equation (6-6).
- Calculate the ACFM as accurately as possible. If necessary, adjust the metered flow rate for differences in pressure, temperature, and molecular weight between the meter specification sheet and actual conditions.
- Make sure that the gas composition is known since it can affect variables such as molecular weight, calculated head, temperature difference between the suction and discharge, and flow rate in lbs/hr.

If problem solving involves a plant test on a centrifugal compressor, beware of increasing the speed at constant volumetric flow. Since the surge point normally increases with speed, the compressor could go into surge if the volumetric flow rate is maintained constant when speed is increased.

Similar guidelines are also appropriate for positive displacement compressors except that there will not be a head versus flow curve as for a centrifugal compressor. It will be important to have instruments calibrated and to know the gas composition so that the actual capacity can be compared to the predicted capacity. The calculated compression exponent can also be compared to those supplied by the compressor manufacturer.

As indicated earlier, restrictions between the pressure measurement points (discharge or suction) can cause the actual pressures in the compressor cycle to be different from the measured pressures. This could cause the compression exponent calculated from inlet and outlet temperatures to be higher than anticipated. In a reciprocating compressor, the most likely cause of this difference in pressures is ribbon valves that are partially plugged. These valves can also cause a loss of compression capacity if they are partially plugged or if they are leaking. This problem can be monitored and detected by using equation (6-8). Chronic valve malfunction is often due to liquid or solids entrainment.

Pumps

One of the most common problems causing poor pump performance is an inadequate available NPSH. While there may be pump manufacturers that claim that their pumps have minimal required NPSH, it should be recognized that all pumps have significant NPSH requirements. The problem solver should look with suspicion on any claims that the NPSH requirements are less than those shown in Table 6-1.

In resolving a centrifugal pump problem, the centrifugal pump performance curve supplied by the pump manufacturer should be used to analyze the problem. If the pump is operating as predicted by the performance curve, then the problem is related to high flow rates or piping limitations. If the pump is not operating on the performance curve, then one of the following five things may be occurring:

- 1. The pump clearances may have worn so that a large amount of liquid is recirculating from the discharge to the suction. This will cause the pump

Table 6-1 Minimum NPSH requirements

Pump Type	NPSH Required, Feet
Centrifugal	6
Centrifugal with booster	1 to 2
Positive displacement	4

to actually be pumping more fluid than shown by flowmeters which will result in a lower than anticipated discharge pressure.

2. The $NPSH_A$ is not sufficient. If there is not sufficient NPSH available, some of the liquid will vaporize in the pump inlet causing the actual amount of liquid being pumped to decrease.
3. A vortex is being formed in the suction side storage tank due to the high velocity in the suction line. The vortex causes vapor to be sucked into the pump suction line. This will cause the pump performance to be below predicted even if the NPSH is sufficient. This problem can be remedied with the installation of a vortex breaker or larger suction line.
4. The pump impeller is the wrong size. Essentially all centrifugal pumps can be fitted with impellers of different sizes. Often during routine maintenance, a new impeller of the wrong size is installed in the pump. It should also be noted that most pump curves show multiple impeller sizes. Thus before the problem solver can accurately consider a pump problem, he needs to know the impeller size that is installed in the pump under consideration.
5. The pump is being driven by a steam turbine and it is not running at the design speed. While this is obviously a steam turbine or steam supply problem, it is often presented to the problem solver as a pump problem.

As indicated for compressors, all instruments should be calibrated and adequately compensated for non-design conditions before beginning to collect any data. The problem solver should also be concerned about pumps operating too far from their design point. If a pump is operating at very low flow rates, the resulting instability may cause damage to the pump internals. In addition, high flow can result in excessive $NPSH_R$ or excessive horsepower requirements.

Positive displacement pump problems often are either related to inadequate available NPSH or leaking check valves. The calculation of available NPSH for a reciprocating pump was discussed earlier. Leaking check valves in reciprocating pumps result in a similar loss in capacity as described for reciprocating compressors.

6.9 EXAMPLE PROBLEM 6-1

A centrifugal compressor (C-100L) handling a gas stream that is mostly nitrogen does not “seem to have” the required process capacity according to operations personnel. The compressor is driven by a steam turbine. The problem solver associated with this plant, was asked to determine the cause of the problem and to recommend actions to get the compressor back up to capacity as soon as possible.

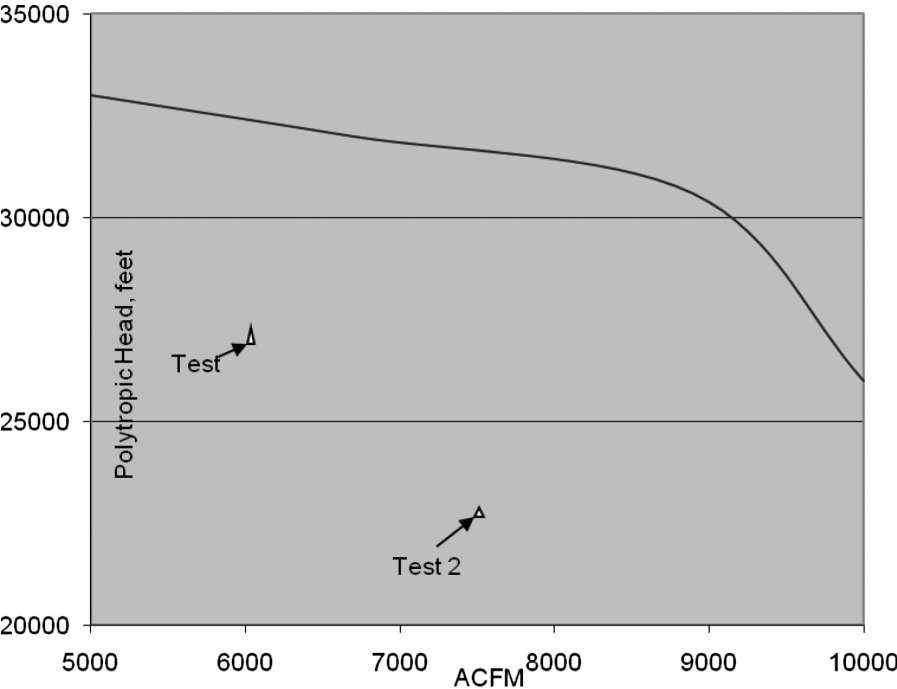


Figure 6-7 Compressor performance curve.

Table 6-2 Compressor data

Variable	Run 1	Run 2
Pressure, psig		
Suction	5	5
Discharge	28	24
Temperature, °F		
Suction	100	100
Discharge	308	300
Flow, lbs/hr	33100	41300

Given:

- The compressor curve (Figure 6-7) is available from the compressor vendor.
- Gas molecular weight = 28.
- Gas compressibility (z) = 1.
- Gas specific heat ratio ($k = C_p/C_v$) = 1.4.
- Plant conditions as shown in Table 6-2. All instruments were calibrated prior to taking any of the data.

In analyzing the problem, the problem solver used the five-step procedure described earlier. He recognized in the words of the operations personnel that they believed the compressor was not performing as it should, but they had not compared the actual compressor performance to the predicted performance.

Step 1: Verify that the Problem Actually Occurred

The problem solver decided that in order to verify the problem that he had to review the compressor performance in detail. So he included the verification step in the problem statement step.

Step 2: Write Out an *Accurate* Statement of What Problem You Are Trying to Solve

The problem statement that he developed was as follows:

“Plant personnel indicate that the performance of C-100L is not as good as they remember from the past. The performance of this compressor is causing a production limit which does not seem to be easily overcome. Determine if the compressor is performing as predicted by the compressor manufacturer’s performance curve. If it is not performing as predicted, determine what the cause of the problem is and recommend remedial actions.”

Note that the above statement emphasizes determining if a problem exists compared to the statement provided by operations personnel which says determine what the problem is. Problem-solving Steps 3 to 5 are not initiated until the alleged poor compressor performance can be verified.

To determine whether C-100L was performing as predicted by the performance curve, the problem solver proceeded and developed Table 6-3.

A reasonable conclusion is that C-100L is performing well below the performance curve at the higher flow rate, and is somewhat below the performance curve at the lower rate. In addition to the poor operation relative to the performance curve, the polytropic efficiency is lower at the higher rates. The actual operating points along with the predicted operating curve are shown in Figure 6-7.

If sufficient data are available, it may be of value to consider when the problem began. The next step is as follows:

Step 3: Develop a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible

Referring back to the list of questions given in Chapter 5, the problem solver developed the questions and answers shown in Table 6-4.

Note that in formulating answers to the questions, the operator’s memory of past performance being better than current performance is not taken as a

Table 6-3 Compressor calculation steps

1. He calculated σ using equation (6-8).		
$T_d = T_s * R^{\sigma}$		
	Run 1	Run 2
Compression ratio	2.17	1.96
Compression exponent (σ)	0.408	0.452
2. He calculated the polytropic head using equation (6-6).		
$H = 1545 * T_s * Z * (R^{\sigma} - 1) / M\sigma$		
Polytropic head, feet	28110	24400
3. He calculated the ACFM (actual cubic feet per minute) at C-100L suction.		
Gas Density, lbs/ft ³	0.0919	0.0919
ACFM	6000	7490
4. He looked up the predicted polytropic head from Figure 6-7.		
Polytropic head, feet	32000	31500
5. He compared the predicted versus actual polytropic heads, and expressed these values as a percent.		
$(\text{Actual-Curve}) * 100 / \text{Curve}$	-12	-23
6. He calculated the polytropic efficiency using equation (6-7) and knowing the compression exponent from Step 1 and the specific heat ratio of 1.4.		
$\sigma = (k - 1) * 100 / (k * E)$		
$(k - 1) / k$	0.286	0.286
Polytropic efficiency	70	63
7. He calculated fluid horsepower required using equation (6-9).		
$\text{BHP} = F * H * 100 / (33000 * E)$		
Horsepower	672	805

fact. If the operator's memory was taken as factual, the possibility of design or construction errors could be eliminated. Memory that is not backed up by hard data is very elusive.

Based on the answers to the questions in Table 6-4, some possible explanations for the problem were proposed as follows:

1. The suction or discharge piping between the pressure gauges and the compressor is either restricted or too small.
2. There is a restriction in the compressor suction inlet or discharge outlet piping.
3. The steam turbine driving the compressor is slowing as the compressor horsepower increases.
4. There may be large amounts of compressor internal leakage allowing gases to flow from the discharge to suction side.

Hypothesis 3 was eliminated since the compressor polytropic efficiency decreases with increasing flow rate. An inadequate steam turbine would not

Table 6-4 Questions/comments for Problem 6-1

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed.
Are all instruments correct?	The instruments had allegedly been calibrated.
Are laboratory results correct?	A gas analysis confirmed the molecular weight of the gas.
Were there any errors made in the original design?	The piping might not have been designed for the high rates. However, this would not explain subpar operation at the lower rates.
Were there changes in operating conditions?	No.
Is fluid leakage occurring?	Internal leakage might explain the problem. In addition, the presence of solids might cause a restriction in the suction piping.
Has there been mechanical wear that would explain the problem?	Mechanical wear of internals might explain the problem.
Is the reaction rate as anticipated?	Not applicable.
Are there adverse reactions occurring?	Not applicable.
Were there errors made in the construction?	Restrictions in the suction or discharge piping associated with construction might explain the problem.

cause the decrease in polytropic efficiency. Hypothesis 4 was treated as a lower priority possibility even though it would explain a reduced polytropic efficiency. However, it is unlikely to explain why the efficiency decreases as flow rate increases. The problem solver decided to test both hypotheses 1 and 2 since they were both theoretically sound working hypotheses. Since he was testing both hypotheses, he postponed formalizing the final working hypothesis until he had done additional work.

Step 4: *Provide a Mechanism to Test the Hypothesis*

Several methods were developed to test these hypotheses. These tests and the results were as follows:

1. The problem solver calculated the pressure drop in the compressor suction and discharge lines between the pressure instruments and compressor inlet and outlet flanges. These calculations indicated that the calculated pressure drop was minimal in both lines. Thus, he felt like hypothesis 1 could be eliminated.

2. After the pressure drop calculations were made, he arranged for X-rays of the suction and discharge piping to be taken. Based on these X-rays, there appeared to be a significant buildup of solids and/or debris on the bottom of the suction piping before and after the suction pressure instrument.
3. The historical data were reviewed to determine the relationship of the compressor efficiency with time. This relationship is shown in Figure 6-8. It is obvious from this figure that there appears to be a single event in time where the efficiency dropped dramatically. A review of operating data indicated an upset in the suction knockout drum that might have caused large amounts of solids to be entrained.

Based on this information, the problem solver developed the following working hypothesis:

“The loss of capacity of C-100L appears to be due to the accumulation of solids in the suction piping. This accumulation of solids is after the suction pressure gauge. The reduced suction pressure is causing the compressor to appear to operate well below the performance curve at the high rates and 12% below the compressor curve at the lower rates. This reduced suction pressure is also causing an apparent loss in compressor efficiency that is more noticeable at high rates. The loss in performance is more noticeable at high rates because the pressure drop caused by the restriction is greater. The presence of solids in the piping may be related to an upset that occurred in the compressor suction drum.”

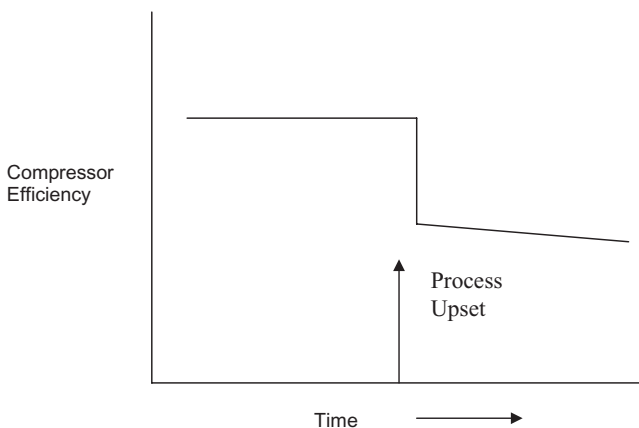


Figure 6-8 Compressor efficiency versus time.

Step 5: *Recommend Remedial Action to Eliminate the Problem without Creating Another Problem*

Since the X-rays indicated the likely presence of solids is the most reasonable cause of the loss of compressor capacity, plans were formulated to shut down the system and clean out the suction piping. While cleaning out the suction piping did eliminate the current compressor limitation, additional problem-solving effort was required. The problem solver next reviewed the upset that appeared to cause solids to be entrained and developed means to prevent this from happening again.

6.10 LESSONS LEARNED

Problems should always be investigated in as quantitative fashion as possible. For example in this problem, the first thing that the problem solver did after developing the problem statement was to determine where the compressor was operating relative to an absolute criteria such as the head-flow curve provided by the compressor manufacturer. It would have been possible to launch into a hypothesis development period before comparing the actual operation to the predicted head curve. However, it would have led to giving equal validity to erroneous hypotheses and valid hypotheses. For example, it was only when the predicted and actual performances were compared at high and low rates that hypotheses 3 and 4 (that there was internal leakage and that the steam turbine was slowing down) could be eliminated.

While hypotheses 1 and 2 were equally valid and could well have been pursued in parallel, it is almost always faster to make calculations to confirm a hypothesis rather than to arrange for elaborate testing. The calculations of pressure drop in the suction piping indicated that the additional cost and time associated with X-raying the suction piping was indeed of value.

This problem also illustrates the flexibility of the five-step approach. The problem solver did not feel that he had sufficient data to propose a hypothesis until he had done some additional work (Step 4) including calculations and X-rays. The five-step approach should not be used to fit all problem-solving activities into a single exact method.

6.11 EXAMPLE PROBLEM 6-2

A process that had been idled for 12 months due to a decrease in demand was now required to operate at full rates. A centrifugal pump (P-25) in the process operated as anticipated until the design flow rate was approached. At that point, it no longer operated as predicted by the pump curve. As the unit was returned to full capacity, the level in the accumulator drum upstream of the pump had been decreased to provide for more surge capacity at the higher

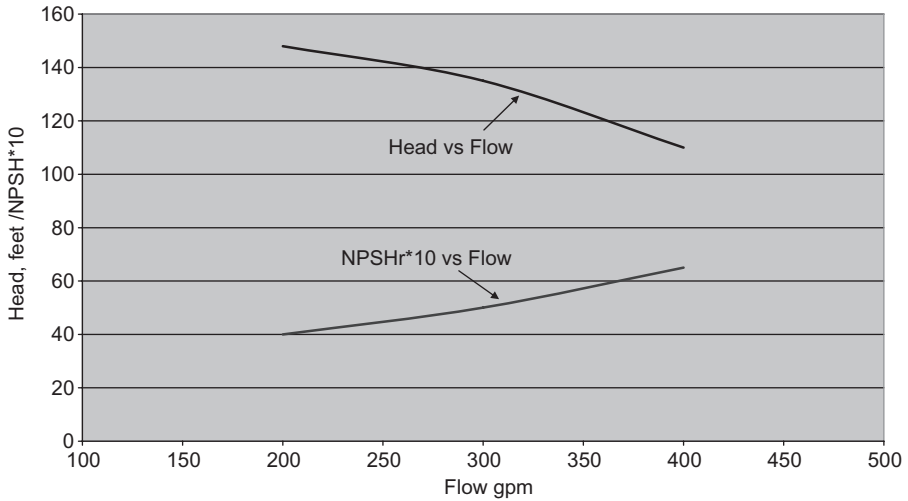


Figure 6-9 Head and $NPSH_R$ for Problem 6-2.

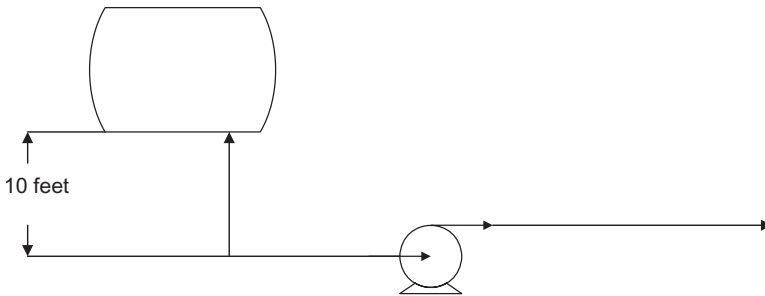


Figure 6-10 Schematic flow for Problem 6-2.

rates. The pump curve is shown in Figure 6-9. The pump was handling a liquid hydrocarbon at its vapor pressure. A schematic flow sheet for the process is shown in Figure 6-10. Operations personnel requested the problem solver determine why the pump fails to perform at design conditions.

Given:

- The pump curve shown in Figure 6-9
- Plant test data shown in Table 6-5
- Liquid Specific Gravity = 0.7
- Hydrocarbon Vapor Pressure = 40 psig
- Pressure Drop in pump suction line = $0.0000528 * F^{1.8}$. Where F = flow rate in gpm.

Table 6-5 Plant test data

Test	Run 1	Run 2	Run 3
Flow rate, gpm	200	300	400
Drum pressure, psig	40	40	40
Pump discharge, psig	88	83	65
Drum liquid level, feet	3	3	4

In analyzing the problem, the problem solver used the five-step procedure described earlier. He combined the first two steps as shown below into a problem statement.

Step 1: Verify that the Problem Actually Occurred

Step 2: Write Out an *Accurate* Statement of what Problem You Are Trying to *Solve*

The problem statement that he developed was as follows:

“P-25 has been reported to be operating off the pump curve as the design flow rate is approached. It is probable that this problem was only noticed as the design rates were required after a 12 month period of low rate operation. The level in the accumulator was decreased when the unit was returned to full rates. Since this pump is creating a major production limitation, work to investigate the problem is planned. The first step will be to confirm that P-25 operates on the pump manufacturer’s pump curve until the design rate is approached. If the pump does not operate on the curve at all rates, determine the cause of the inadequate performance.”

To confirm whether P-25 is operating on the vendor pump curve, the problem solver did the calculations shown in Table 6-6.

The problem solver concluded that P-25 was operating close to the pump curve until the flow rate reached 400 gpm. The next step was:

Step 3: Develop a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible

Again the questions given in Chapter 5 were helpful to the problem solver in formulating possible hypotheses. These questions and appropriate comments developed by the problem solver for this example problem are shown in Table 6-7.

Based on this series of questions, two possible hypotheses were developed as follows:

1. The suction piping is too small or is restricted causing insufficient NPSH at the pump inlet flange.

Table 6-6 Performance calculations

	Run 1	Run 2	Run 3
1. He calculated the pressure at the pump suction using the relationship given between flow and pressure drop.			
Suction line pressure drop, psi	0.732	1.52	2.55
Elevation head, psi	3.94	3.94	4.25
Suction pressure, psig	43.2	42.4	41.7
2. He calculated the pump differential head knowing the specific gravity relative to water was 0.7.			
Discharge pressure, psig	88	83	65
Differential pressure, psig	44.8	40.6	23.3
Differential head, feet	148	134	77
3. He compared the actual to predicted differential pressure expressed as a percentage.			
Curve differential head, feet	148	135	110
Error, percent	0	0.7	30

Table 6-7 Questions/comments for Problem 6-2

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed. The operating directive for the level in the drum had recently been reduced.
Are all instruments correct?	The instruments had allegedly been calibrated.
Are laboratory results correct?	Not applicable.
Were there any errors made in the original design?	The piping might not have been designed for the high rates or the increasing $NPSH_R$ as the flow increased might not have been considered.
Were there changes in operating conditions?	No except for the increased flow and reduced level.
Is fluid leakage occurring?	Internal leakage might explain the problem.
Has there been mechanical wear that would explain the problem?	Deterioration of wear rings might explain the problem.
Is the reaction rate as anticipated?	Not applicable.
Are there adverse reactions occurring?	Not applicable.
Were there errors made in the construction?	Not applicable. There had been no recent construction.

Table 6-8 Pump calculations for Problem 6-2

	Run 1	Run 2	Run 3
Vapor pressure of liquid, psig	40	40	40
Suction pressure at pump from Table 6-6, psig	43.2	42.4	41.7
NPSH available, psi	3.2	2.4	1.7
NPSH available, feet	10.5	7.9	5.6
NPSH required, feet			
From curve	4	5	6.5
Safety factor	0.5	0.5	0.5
Total	4.5	5.5	7

2. Deterioration of internal pump wear rings might be causing internal leakage so that the pump is recirculating large quantities of fluid. This will cause the pump to appear to be operating off the performance curve.

Following the concept of doing calculations prior to making recommendations to do mechanical work, the calculations shown in Table 6-8 were done.

Since at the highest rate (400 gpm) the NPSH_R (7 feet including the safety factor) is greater than the NPSH_A (5.6 feet), the problem solver developed the following working hypothesis:

“The failure of P-25 to operate on the pump curve at high rates is due to the fact that the NPSH is not sufficient.”

Step 4: *Provide a Mechanism to Test the Hypothesis*

The problem solver developed two mechanisms to test the hypothesis. The suction line could be replaced to reduce the pressure drop in the suction line. A larger suction line that reduced the pressure drop to less than 1 psi would increase the NPSH_A to a value above that required by the pump. Another possible mechanism to test the hypothesis would be to raise the level in the drum. If the level were increased by at least 1.5 feet, the NPSH_A should be adequate.

Step 5: *Recommend Remedial Action to Eliminate the Problem without Creating Another Problem*

The remedial action depends on which of the hypothesis testing mechanisms is used. If the suction line is replaced and the problem is eliminated, this mechanism becomes the remedial action. If raising the drum level is a successful test, this may or may not be a remedial action. Raising the drum level reduces the amount of surge volume that can be used. A careful study would be required to determine if this action creates other problems.

6.12 LESSONS LEARNED

While the available data did not allow the problem solver to eliminate the hypothesis that there was a mechanical problem with the pump that allowed it to recirculate large amounts of fluid, he could by calculations show that the hypothesis of inadequate available NPSH was a correct hypothesis. Thus if the pump had no mechanical problems at all, it still would not perform as predicted by the pump curve. Therefore, the problem solver elected to develop solutions to the lack of available NPSH.

Often in a process unit, operating directives that are changed and seem to work fine at reduced rates are not adequate when the rates are increased to design levels. In addition, designs that work at less than design rates, may not work at full rates. In the specific example problem, the reduction in the drum level seems to be the cause of the lack of available NPSH. However, additional study would be required before raising the drum level would be considered an acceptable solution.

6.13 EXAMPLE PROBLEM 6-3 (THIS PROBLEM IS PROVIDED TO ILLUSTRATE A CALCULATION TECHNIQUE)

A reciprocating compressor (C-100A) was operating in a mode that results in an overload condition on the electric motor. The compressor was equipped with adjustable clearance pockets so that the clearance as a fraction of displacement could be varied. What clearance pocket setting should be used to obtain the maximum flow rate without overloading the electric motor?

Given:

• Clearance pocket setting, percent of displacement	4 or 6 or 10
• Suction pressure, psig	15
• Discharge pressure, psig	85
• Compressibility factor (z)	1
• Molecular weight	42
• Polytropic compression exponent	0.32
• Suction temperature, °F	100
• Ratio of specific heats	1.4
• Polytropic efficiency	90
• Mechanical efficiency	95
• Piston displacement, ft ³ /minute	300
• Motor rating, HP	55

The following procedure shown in Table 6-9 can be used to analyze this problem:

Table 6-9 Calculation procedure

1. Calculate the compression ratio:

$$R = 99.7/29.7 = 3.36 \quad (6-18)$$

2. Calculate the polytropic head using equation (6-6):

$$H = 1545 * T_s * Z * (R^a - 1) / M\sigma$$

$$H = (1545 * (100 + 460) * 1 * (3.36^{0.32} - 1)) / (42 * 0.32) = 30500 \text{ feet} \quad (6-19)$$

3. Calculate the volumetric efficiency for each clearance using equation (6-14):

$$E_v = 100 * (1 - L - C * (R^{1/k} - 1))$$

The leakage factor (L) can be evaluated as 2 percent of the compression ratio as follows:

$$L = 2 * R / 100 = 0.07 \quad (6-20)$$

Clearance, percent	4	6	10
Clearance factor (C)	0.04	0.06	0.10
Leakage factor (L)	0.07	0.07	0.07
$R^{1/k} - 1$	1.38	1.38	1.38
Volumetric efficiency, percent	87	85	79

4. Calculate the mass flow rate and BHP. Use equation (6-9) to calculate the BHP:

$$BHP = F * H * 100 / (33000 * E)$$

Volumetric flow rate, ft ³ /minute	261	255	237
From piston displacement and volumetric efficiency			
Gas density, lbs/ft ³	0.208	0.208	0.208
Mass flow rate, lbs/minute	54.3	53	49.3
BHP	58.7	57.3	53.3

Note the BHP includes both mechanical and polytropic efficiency.
 Conclusion: The 10 percent pocket setting must be used to avoid overloading the motor.

6.14 EXAMPLE PROBLEM 6-4

The compressor described in Problem 6-3 began losing capacity. The flow-meter showed about 35 lbs/minute. Estimates of motor loading based on ampere readings indicated that the compressor was requiring significantly less than 50 BHP. All operating conditions were identical to those specified in Problem 6-3. In addition, the pocket clearance was set at 10 percent. When the problem solver was asked to consider this problem, he used the five-step approach discussed earlier.

Step 1: Verify that the Problem Actually Occurred

Verification that the problem was actually occurring was relatively simple since both the flowmeter and the ampere reading indicated that the compressor output was less than its rated capacity.

Step 2: Write Out an *Accurate* Statement of What Problem You Are Trying to Solve

The problem solver wrote out the following problem statement:

“C-100A seems to be operating well below the design capacity. The flow meter shows 35lbs/hr where the flow should be close to 50lbs/hr. In addition, the horsepower loading is well below the anticipated load of 50 BHP as determined by an ampere reading. The compressor unloading pockets are set so that the clearance is about 10% which is normal. It is not known when the decrease in capacity actually occurred, but it seems to have been a gradual decrease. Determine what has caused the loss of capacity on C-100A (the reciprocating compressor), why it occurred, and what can be done to eliminate the problem.”

Step 3: Develop a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible

The questions given in Chapter 5 were used to help formulate possible hypotheses. These questions and appropriate comments developed by the problem solver for this example problem are shown in Table 6-10.

Several possible hypotheses were developed by the problem solver as follows:

1. The valves in the compressor are bad causing the loss in capacity.
2. The flowmeter is erroneously low.
3. The worn belt drive between the electric motor and compressor is slipping, causing the compressor to operate at a much lower speed than design.
4. The molecular weight of the gas being compressed is different than design.
5. The actual suction pressure is much lower than shown by the instrumentation.

The problem solver developed a table to attempt to sort out the various hypotheses by comparing the theoretical impact of the hypotheses to the actual observations. This table is shown in Table 6-11.

Since “slipping belts” (hypothesis 3) will almost always be heard even above the noise in a compressor house, the problem solver proposed the residual theoretically sound working hypothesis as follows:

Table 6-10 Questions/comments for Problem 6-4

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed.
Are all instruments correct?	All instruments except the flowmeter had been calibrated.
Are laboratory results correct?	Analysis of gas being compressed had not been obtained for several months.
Were there any errors made in the original design?	Not applicable since the compressor capacity loss was a recent occurrence.
Were there changes in operating conditions?	No.
Is fluid leakage occurring?	Internal leakage might explain the problem.
Has there been mechanical wear that would explain the problem?	Deterioration of compressor valves might explain the problem. In addition, the belt on the electric motor was beginning to look worn.
Is the reaction rate as anticipated?	Not applicable.
Are there adverse reactions occurring?	Not applicable.
Were there errors made in the construction?	Not applicable.

Table 6-11 Hypothesis comparison

Hypothesis (number)	Would hypothesis Explain Observations of:	
	Low Ampere Reading	Low Flow Rate
Bad valves (1)	Yes	Yes
Flowmeter (2)	No	Yes
Slipping belt (3)	Yes	Yes
Molecular weight (4)	No ⁽¹⁾	?
Low suction pressure (5)	? ⁽²⁾	Yes

(1) For a reciprocating compressor, the horsepower load is essentially independent of molecular weight. This is true because head is indirectly related to molecular weight (see equation (6-6)), and the mass rate is directly related to the molecular weight. For example, if the molecular weight of a gas being compressed doubles, the polytropic head will be reduced by a factor of 2 and the amount of gas being compressed will increase by a factor of 2. This assumes that the suction and discharge pressures are constant and the only change is the molecular weight of the gas.

(2) Whether or not a low suction pressure can explain the decrease in horsepower requirements depends on which side of the load point the compressor is operating at normal conditions. See Figure 6-6 for a typical load versus suction pressure curve. For this specific compressor, it is likely that decreasing the suction pressure will have minimal impact on the horsepower requirements.

“The poor performance of C-100A is due to leakage through the suction and/or discharge valves.”

Step 4: Provide a Mechanism to Test the Hypothesis

The actual mechanism for testing the hypothesis involved determination of “optimum technical depth” required as described in Chapter 3. Some points that were considered in determining the “optimum technical depth” were as follows:

- How urgent was the problem? Was the loss of capacity causing a loss in plant production or could gases be diverted to another location?
- Was a spare compressor available? If a spare compressor were available, the required degree of confidence that the solution was correct would be less than if no spare was available.
- Would a compressor shutdown require an entire unit shutdown? If a unit shutdown were required, the required degree of confidence would be much higher.
- Could inlet and outlet temperatures be easily measured and were historical data available? If these temperatures could be easily obtained and compared to historical data, it would increase the degree of confidence in the solution.

The two possibilities were that the current and historical inlet and outlet temperatures were easily available. In this case, the compression exponent could be calculated using equation (6-8) as shown below:

$$T_d = T_s * R^\sigma \quad (6-8)$$

Then, archived data could be used to calculate the historical compression exponent (σ). The current data could be compared to historical data and if a change were obvious, it could be concluded that this was a valid test of the hypothesis. If no historical data are available, equation (6-7) can be used to calculate the theoretical compression exponent from the vendor’s performance curve.

$$\sigma = (k - 1) * 100 / (k * E) \quad (6-7)$$

This theoretical compression exponent can then be compared to the actual exponent based on plant operating data. If compressor inlet and outlet temperatures are not readily available, it may be possible to use infrared techniques discussed in Chapter 10 to approximate compressor temperatures.

In this particular problem, a spare compressor was not available. An analysis of the inlet and outlet temperatures indicated that the deterioration of

Table 6-12 Analysis of compression exponent for Problem 6-4

		Days after Last Valve Replacement			
Variable	Design	0	30	60	90
Suction					
Temperature, °F	70	70	70	70	70
Pressure, psig	15	15	15	15	15
Discharge					
Temperature, °F	320	320	331	340	360
Pressure, psig	85	85	85	85	85
Compression ratio	3.36	3.36	3.36	3.36	3.36
Compression exponent	0.32	0.32	0.33	0.34	0.36

performance had been a gradual decline. This analysis is shown in Table 6-12.

Step 5: Recommend Remedial Action to Eliminate the Problem without Creating Another Problem

Thus unfortunately, it was necessary to recommend a compressor shutdown to replace the worn valves. Since there was no spare compressor and the compressor was an integral part of the unit, it was necessary to shut down the entire unit. As seems to be the rule, the shutdown occurred at a bad time from a business perspective.

6.15 LESSONS LEARNED

Replacement of valves on a reciprocating compressor is a “normal maintenance” item. However, since this compressor was in a critical service, the problem solver developed a system to allow including the compression exponent in a daily monitoring system. His recommendation to do this allowed optimization of the timing for a compressor downtime. In addition, it allowed him to follow the valve performance closely and to possibly correlate valve performance with process upsets or changes that are causing rapid valve wear.

The importance of understanding technology is also illustrated by this problem. The original hypothesis that a change in molecular weight of the gas being compressed was eliminated because a reciprocating compressor horsepower is essentially independent of molecular weight. In addition, the possibility that a low suction pressure is causing the problem was eliminated since with this specific reciprocating compressor, suction pressure has minimal affect on horsepower load. These conclusions are not intuitively obvious and can only be developed by understanding compression technology.

6.16 EXAMPLE PROBLEM 6-5 (THIS PROBLEM IS PROVIDED TO ILLUSTRATE A CALCULATION TECHNIQUE)

Determine the $NPSH_A$ for a reciprocating pump given the following:

• Pump type	double acting
• Cylinder Diameter	1/2 inch
• Stroke length	4 inches
• Speed	60rpm
• Suction line diameter	1 inch
• Suction line length	25 actual feet
• Suction drum pressure	40 psig
• Liquid elevation	10 feet above pump suction
• Fluid vapor pressure	40 psig
• Fluid Specific Gravity	0.65 relative to water
• Fluid viscosity	0.2 centipoise

As indicated in Section 6.6, there are two kinds of pressure drop in the suction line of a reciprocating pump. There is the typical type of frictional loss, but it occurs at maximum flow rate which is greater than the average flow rate. In addition, the entire volume of fluid in the suction piping must be accelerated from a non-flow condition to the maximum velocity. As indicated in this section, these two frictional losses occur completely out of phase with each other. That is, the frictional loss associated with the maximum flow rate occurs when there is no acceleration. And the acceleration loss from zero velocity to full line velocity occurs when there is no frictional loss. Thus, the pressure loss in the pipe is generally taken as the larger of the two calculated values. The calculations for estimating these pressure losses are based on equations (6-11) and (6-12). The calculation procedure is as follows:

1. Calculate the maximum flow rate in the suction pipe:

$$V_P = K * D^2 * L * S / (60 * D_P^2) \quad (6-11)$$

$$= \pi * (0.0417^2) * 0.33 * 60 / (2 * 60 * (0.0833^2))$$

$$= 0.13 \text{ fps} \quad (6-21)$$

2. Calculate the frictional pressure drop by conventional means. This calculation is not shown.

$$h_F = 0.0069 \text{ feet}$$

3. Calculate the head required to accelerate the fluid.

$$h_A = 1.35 * L_P * S * V_P / 307 \quad (6-12)$$

$$= 1.35 * 25 * 60 * 0.13 / 307$$

$$= 0.85 \text{ feet} \quad (6-22)$$

4. Select the larger of the two values to determine the actual NPSH for the system.

In this specific problem, the acceleration head will be the critical pressure loss. Actual NPSH at the pump suction will be 10 feet less 0.85 feet or 9.15 feet. This available NPSH will normally be adequate for most reciprocating pumps.

6.17 EXAMPLE PROBLEM 6-6

A centrifugal process gas compressor C-5A driven by a steam turbine no longer had sufficient capacity for the service that it was designed for. The speed of the turbine was controlled by a steam control valve in the incoming steam. There had allegedly been no changes in operating conditions except for a decrease in steam pressure from 200 to 190 psig. This decrease in steam pressure was part of an overall optimization of the plant utility system. In order to increase the steam pressure slightly, operations personnel removed the steam meter orifice that was used to measure the steam flow to the steam turbine. Operations personnel had requested technical help to prove that the steam pressure should be increased back to 200 psig.

The design and current operating conditions are shown in Table 6-13.

The maximum design of the steam turbine included a slight safety factor to allow operations at 10000rpm with the steam control valve 90 percent open. As noted in the table even with the steam valve 100 percent open, it is not possible to reach 9000rpm. The design conditions are those required for the process gas compressor.

The problem solver approached the problem using the five-step procedure as shown below.

Step 1: Verify that the Problem Actually Occurred

As the first step in verifying that the problem was real, the problem solver had the appropriate instruments checked. He also used independent sources to confirm the flow and pressure meters. While the compressor output had not been followed on a daily basis, key variables shown in Table 6-13 were available from computer archives. All of these indicated that there was a real problem.

Table 6-13 Design and current operations

Variable	Design	Current Operations
Suction pressure, psig	5	5
Discharge pressure, psig	45	35
Suction temperature, °F	100	100
Discharge temperature, °F	301	264
Flow rate, lbs/hr	25000	25000
Gas composition		
Propylene, mol percent	95	95
Nitrogen, mol percent	5	5
Calculated molecular weight	41.3	41.3
Compressibility	1.0	1.0
Specific heat ratios		
Propylene	1.21	1.21
Nitrogen	1.4	1.4
Mixture	1.2195	1.2195
Turbine speed, rpm		
Maximum	10000	10000
Design	9000	
Actual		8400
Inlet steam conditions		
psig	200	190
Temperature, °F	500	485
Outlet steam conditions		
psig	25	25
Temperature, °F	280	295
Steam flow rate, lbs/hr		Out of service
Maximum	16000	
Design	14700	
Steam control valve		
Position, percent	80	100

Step 2: Write Out an *Accurate* Statement of What Problem You Are Trying to *Solve*

The problem solver wrote out a description of the problem that he was trying to solve as follows:

“Currently C-5A does not seem to have the desired capacity, even though capacity was adequate in recent history. The steam turbine is operating at slightly lower speed than the design values and the steam control valve is fully open. There has been a reduction in inlet steam pressure from 200 psig to 190 psig. However, it is not clear that this is the cause of the lack of capacity. Determine why C-5A does not have sufficient capacity and provide recommendations for improving the performance of C-5A.”

Step 3: *Develop* a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible

The questions given in Chapter 5 were helpful in formulating possible hypotheses. These questions and appropriate comments for this example problem are shown in Table 6-14.

Several hypotheses were proposed as follows:

- When the steam system was optimized, the process designer did not adequately consider the impact of the steam pressure on the steam turbine.
- There is excessive leakage around the wear rings on the process gas compressor. This excessive leakage would cause a lower than design compressor efficiency and a reduced gas rate.
- The steam turbine steam jets may have deteriorated. This would cause the steam turbine to have a lower efficiency and thus extract less horsepower per pound of steam than it was designed to do.

Table 6-14 Questions/comments for Problem 6-6

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed except for the lower steam pressure.
Are all instruments correct?	All instruments except the steam flowmeter had been calibrated.
Are laboratory results correct?	Laboratory results indicating that the gas being compressed was 95 percent propylene and 5 percent nitrogen were confirmed.
Were there any errors made in the original design?	The original design was ok, but there was a question about whether the change in steam pressure had received adequate consideration.
Were there changes in operating conditions?	Yes. The inlet steam pressure was reduced.
Is fluid leakage occurring?	Internal leakage might explain the problem.
Has there been mechanical wear that would explain the problem?	Deterioration of the steam turbine nozzles might explain the problem.
Is the reaction rate as anticipated?	Not applicable.
Are there adverse reactions occurring?	Not applicable.
Were there errors made in the construction?	Not applicable.

At this point, the problem solver had developed three theoretically correct working hypotheses. All of the three could be evaluated further by additional calculations. Since two of the hypotheses would require compressor shut-downs to inspect and the compressor was not spared, he elected to pursue additional calculations as part of Step 4.

Step 4: Provide a Mechanism to Test the Hypothesis

The problem solver made the following calculations to help determine if one of these proposed hypotheses was both possible and supported by calculations.

1. He determined the polytropic compression exponent using equation (6-8) as shown in Table 6-15:

$$T_d = T_s * R^\sigma \quad (6-8)$$

Since the polytropic compression exponent is the same for the design and operating conditions, the problem solver concluded based on equation (6-7) that the compressor efficiency was the same as the design efficiency.

$$\sigma = (k - 1) * 100 / (k * E) \quad (6-7)$$

2. He calculated the steam turbine efficiency using equation (6-17) and Table 6-16:

$$E_T = 100 * (H_I - H_O) / (H_I - H_E) \quad (6-17)$$

It is of value to review how the calculations shown in the table were actually done. The inlet and outlet steam enthalpies were taken from steam enthalpy tables given in multiple publications. These values were used to determine the actual enthalpy change across the turbine. The value shown in the table as “at

Table 6-15 Calculation of polytropic compression exponent

Variable	Design	Operating
Suction pressure, psig	5	5
Discharge pressure, psig	45	35
Suction temperature, °F	100	100
Discharge temperature, °F	301	264
Calculated compression ratio	3.03	2.52
Polytropic compression expon.	0.277	0.278

Table 6-16 Calculation of steam turbine efficiency

Variable	Design	Operating
Inlet steam conditions		
psig	200	190
Temperature, °F	500	485
Enthalpy, BTU/lb	1267	1260
Outlet steam conditions		
psig	25	25
Temperature, °F	280	308
Enthalpy, BTU/lb	1176	1191
Enthalpy change, BTU/lb		
Actual	91	69
At 100 percent efficiency	140	138
Steam turbine efficiency, percent	65	50
Calculated steam rate, lbs/hr	14700	15800

100 percent efficiency” assumes isentropic (constant entropy) steam expansion. The most efficient steam turbine process is one that occurs at constant entropy. The outlet steam conditions are then based on the outlet pressure and maintaining the same entropy as the inlet steam conditions. The outlet enthalpy is then determined from steam charts or steam tables. The isentropic enthalpy change can then be determined. The efficiency is simply the actual enthalpy change divided by the isentropic enthalpy change and multiplied by 100.

As shown in Table 6-16, the current efficiency of the steam turbine appeared to be less than design. Thus, it seemed unlikely that the current capacity loss was associated with the steam pressure change. Since archived data were available, the problem solver reviewed the historical data to determine when the loss of efficiency occurred and whether it was a one-time loss or a gradual loss. The problem solver used the techniques shown above and developed Figure 6-11. This figure clearly showed that the steam turbine problem was not related to the drop in steam pressure, but was a gradual decay in efficiency that began well after the change in steam pressure.

The problem solver had one more question to answer—that is, would an increase in steam pressure back to 200 psig ameliorate the loss of turbine capacity? To answer this question, he calculated the current horsepower load and compared it to the design horsepower load.

Equations (6-6) and (6-9) shown below and data given in Table 6-13 were used to calculate the polytropic head and fluid horsepower. These equations were then used to develop Table 6-17.

$$H = 1545 * T_s * Z * (R^\sigma - 1) / M\sigma \quad (6-6)$$

$$\sigma = (k - 1) * 100 / (k * E) \quad (6-7)$$

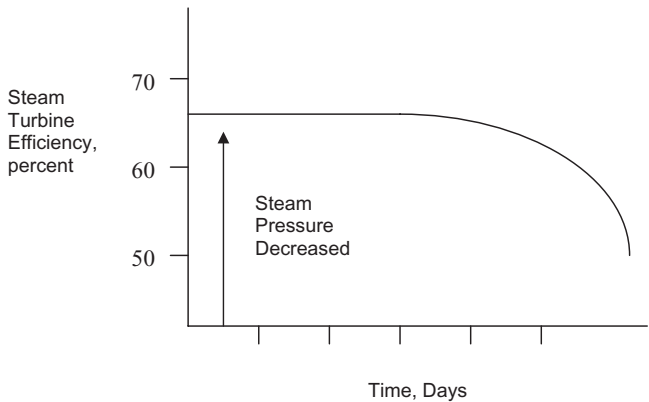


Figure 6-11 Steam turbine efficiency versus time.

Table 6-17 Compressor horsepower calculations

Variable	Design	Operating
Suction pressure, psig	5	5
Discharge pressure, psig	45	35
Suction temperature, °F	100	100
Discharge temperature, °F	301	264
Flow rate, lbs/hr	25000	25000
Polytropic efficiency	65	65
Polytropic compression expon.	0.277	0.278
Calculated polytropic head	27200	22100
Fluid horsepower	530	430

$$\text{BHP} = F * H * 100 / (33000 * E) \tag{6-9}$$

He then considered whether the increase in steam pressure from 190 to 200 psig would cause the compressor to return to normal. To consider this change in steam pressure, the problem solver first estimated the current steam rate knowing the delivered fluid horsepower (430 BHP) and the enthalpy change across the turbine. He then assumed that steam conditions were returned to the higher pressure, the steam rate increased slightly due to the higher pressure and that the turbine efficiency remained the same (50 percent). He then calculated the horsepower that would be delivered to the process as shown in Table 6-18.

Based on the calculations shown in Table 6-18, the problem solver concluded that raising the steam pressure would not significantly increase the capacity of the process gas compressor. He then developed the following hypothesis:

Table 6-18 Calculation of BHP delivered to compressor with increased steam pressure

Variable	Operating Conditions		
	Design	Current	Proposed
Inlet steam conditions			
psig	200	190	200
Temperature, °F	500	485	500
Enthalpy, BTU/lb	1267	1260	1267
Outlet steam conditions			
psig	25	25	25
Temperature, °F	280	308	TBD
Enthalpy, BTU/lb	1176	1191	TBD
Enthalpy change, BTU/lb			
At 100 percent efficiency	140	138	140
Steam turbine efficiency	65	50	50
Actual	91	69	70
Steam rate	14700	15800	16300
Horsepower to process	530	430	450

“It is believed that the steam turbine steam jets have suffered mechanical damage which has resulted in the gradual deterioration of their efficiency. This would cause the steam turbine to have a lower efficiency and thus extract less horsepower per pound of steam than it was designed to do. Increasing the steam pressure from 190 psig to 200 psig would have minimal impact on the turbine.”

Step 5: Recommend Remedial Action to Eliminate the Problem without Creating Another Problem

Since all indications were that there was some sort of mechanical damage to the internals of the steam turbine and that the turbine efficiency was continuing to deteriorate, the problem solver had no choice but to recommend that the steam turbine be shut down for repairs. In addition, the time relationship indicated that the repairs should be done as soon as possible. Since safety did not appear to be involved, the actual timing of the shutdown was left to the discretion of the management team.

The management team was pleased with the detailed analysis of the problem because:

1. The initial apparent cause of the problem (the steam pressure reduction) would have been difficult to reverse since it involved several processes in the plant.
2. The relationship of the turbine efficiency with time that was developed was helpful in determining that the steam turbine should be repaired very quickly.

6.18 LESSONS LEARNED

The value in doing calculations and time-related figures was clearly illustrated by this real-life problem. Before the problem solver could determine which piece of equipment was the source of the problem, he had to determine the performance of both the compressor and turbine. He determined this by comparing the actual efficiency to the design efficiency. Knowing that the compressor efficiency was essentially the same as the design and that the steam turbine efficiency was less than design allowed him to conclude that the operating problem was related to the steam turbine. In addition, an analysis of the steam turbine supply pressure allowed him to conclude that decreasing the steam pressure was not the cause of the problem and that increasing it back to the original setting would not resolve the performance discrepancy.

If these calculations had not been done, there would be three possible hypotheses that would all be treated as valid. Without the calculations, the most easily identified change would be the reduction in steam pressure. It would also appear to be the easiest route to improving performance. If the problem solver had not done the discussed calculations, it is likely that increasing the steam pressure would have been chosen as the route to improve performance. Valuable time that could have been spent in doing a better job in assessing the problem would have been spent in getting the steam pressure raised.

6.19 EXAMPLE PROBLEM 6-7

A new process had recently been put into operation. While the start-up had gone very well, there was a continuing compressor problem. The main recycle gas compressor would mysteriously shut down. The 1500-BHP two-stage reciprocating compressor was driven by an electric motor. This motor was provided with a shutdown device that was triggered if the horsepower load was 3 percent greater than the motor rating. Thus, the compressor motor would shut down if the load exceeded 1550 BHP.

The compressor was provided with a “first out” indicator which was used to determine which process variable caused the electric motor to shut down. The “first out” indicator included process variables such as oil pressure, high discharge temperatures, high suction temperatures and low suction pressure. High suction pressure was not included in the “first out” indicator. However, there was a high suction pressure alarm to provide a warning prior to the pressure increasing to the point that the safety valve would release. The indicator panel also had a category called “other reason”. Unfortunately the indicator almost always showed “other reason” for the shutdowns being experienced.

The process gas load was not constant. The gas load varied as the reactor conversion changed. If the reactor conversion decreased, the gas load

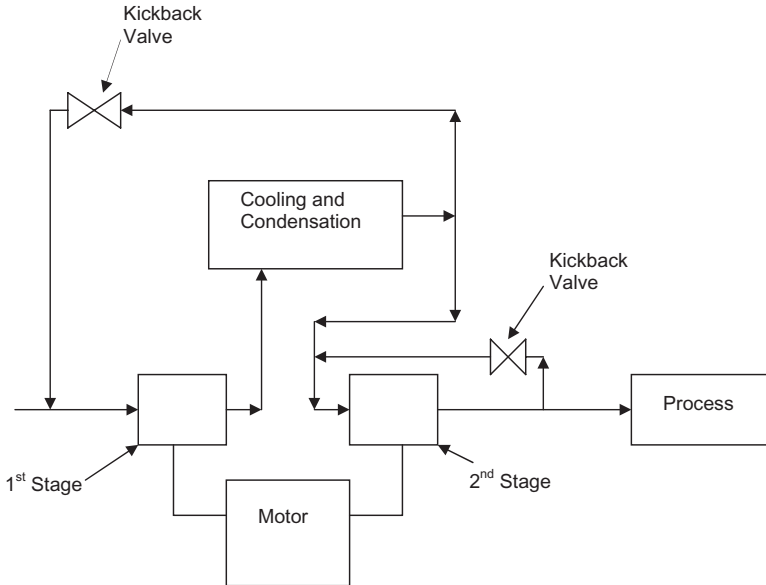


Figure 6-12 Schematic flow for Problem 6-7.

increased. The process design of the facilities assumed that the conversion would remain constant. Decreases in the conversion were associated with the presence of impurities in the reactor feed or changes in the catalyst flow rate to the reactor.

The compressor was provided with computer-controlled unloaders and recycle capabilities to maintain a constant suction pressure on both stages. If the gas load were such that both the recycle valves were closed and the unloaders were in a position to compress the maximum amount of gas, the suction pressure would increase until the gas density increased to the point that the compressor had adequate capacity. A schematic sketch of the facilities is shown in Figure 6-12.

The key variables for the compressor are given in Table 6-19.

Operations personnel have requested help from the technical organization to determine what was wrong with the “first out” indicator. The problem solver approached the problem using the five-step procedure as shown below.

Step 1: Verify that the Problem Actually Occurred

There was no doubt that the compressor was shutting down. However, it wasn't obvious that there was anything wrong with the “first out” indicator. There were times when it showed indications besides “other reason”. In addition, simulated signals were used when the system was out of service to

Table 6-19 Compressor operating data for Problem 6-7

First-stage suction pressure, psig	3
Second-stage suction pressure, psig	60
Interstage pressure drop, psi	2
Discharge pressure, psig	275
Compressibility factor (z)	1
Molecular weight	42
First-stage suction temperature, °F	100
First-stage discharge temperature, °F	283
Second-stage suction temperature, °F	110
Second-stage discharge temperature, °F	280
Interstage condensation, lbs/hr	0
Ratio of specific heats	1.21
Polytropic efficiency	90
Mechanical efficiency	95
Piston displacement, ft ³ /minute	5000
Motor rating, HP	1550 (includes a 3 percent overload factor)

confirm that all other indicators worked. The problem solver expanded the original problem scope and stated it as shown in Step 2.

Step 2: *Write out an Accurate Statement of What Problem You Are Trying to Solve*

“C-122 has been shutting down for no apparent reason. The “first out indicator” shows the cause is “other reason”. At about the same time as the mysterious shutdowns, the suction pressure tends to increase. However, it has been impossible to determine whether this causes the shutdowns or is the result of the shutdowns. Investigate the shutdowns of C-122, the recycle gas compressor, to determine what is causing the unknown shutdowns. There may be a problem with the “first out indicator” or there may be an unknown reason for the compressor shutdowns. When the cause is determined provide recommendations to eliminate the problem.”

Step 3: *Develop a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible*

The questions given in Chapter 5 were used to help formulate possible hypotheses. These questions and appropriate comments for this example problem are shown in Table 6-20.

Based on the above table, the problem solver formulated the following hypotheses:

Table 6-20 Questions/comments for Problem 6-7

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed except there were times when the low-stage suction pressure was not well controlled.
Are all instruments correct?	All pressure instruments had been calibrated.
Are laboratory results correct?	Not applicable.
Were there any errors made in the original design?	Since this was a new process, this was a consideration. However, the major concerns were the “first out indicator” and the capability of the compressor to handle swings in recycle gas rates with subsequent changes in suction pressure.
Were there changes in operating conditions?	No, except for suction pressure swings.
Is fluid leakage occurring?	Internal leakage might explain the failure of the compressor to handle the gas flow under some conditions.
Has there been mechanical wear that would explain the problem?	Leaking compressor valves might explain the problem.
Is the reaction rate as anticipated?	Normally yes. However, decreases in reaction rate cause increased recycle gas rates.
Are there adverse reactions occurring?	Not applicable.
Were there errors made in the construction?	Construction errors in the “first out” system might explain the problem.

1. There is a compressor mechanical problem such as bad valves. This problem is not apparent at low flow rates, but becomes apparent at high rates. This mechanical problem causes the compressor to have insufficient capacity at high gas rates. As the suction pressure increases, the compressor shuts down for some unknown reason.
2. The compressor is shutting down for some unknown reason when the suction pressure rises slightly due to normal process variability.
3. There is an intermittent instrumentation failure with the “first out” system. This failure is causing some problems such as low oil pressure to shut down the compressor, but does not show up on the display panel.

Note that there is similarity between the first and second hypotheses. The first hypothesis implies that there is a mechanical condition that can be repaired and the problem will be eliminated. The second hypothesis indicates that the

Table 6-21 Calculations of compressor efficiency

Variable	Design	Current
Low-stage suction pressure, psig	3	3
Low-stage discharge pressure, psig	62	62
High-stage suction pressure, psig	60	60
High-stage discharge pressure, psig	275	275
Low-stage suction temperature, °F	100	100
Low-stage discharge temperature, °F	278	283
High-stage suction temperature, °F	110	110
High-stage discharge temperature, °F	276	280
Compression exponent (from temperatures)		0.193
Polytropic efficiency, percent	92	90
Polytropic head, feet	67200	67400
Mass flow rate, lbs/minute	620	620
Total horsepower, BHP	1440	1480

mysterious shutdowns are due to process variability and that there is nothing mechanically wrong with the compressor.

When faced with the need to decide which of these hypotheses to pursue, the problem solver recognized that it might be difficult to trace an intermittent instrument failure associated with the “first out” system. On the other hand, it would be possible to quickly do some calculations to confirm whether or not either hypotheses 1 or 2 were theoretically correct. He used the following relationships and the basic data shown in Table 6-19 to develop Table 6-21.

$$T_d = T_s * R^\sigma \quad (6-8)$$

The problem solver used equation (6-8) with the suction and discharge temperatures in absolute temperature units and calculated a compression exponent of 0.193. He then used the compression exponent (σ), the specific heat ratio and equation (6-7) shown below to calculate the polytropic efficiency. The ratio of specific heats is given in Table 6-19.

$$\sigma = (k - 1) * 100 / (k * E) \quad (6-7)$$

As shown in Table 6-21, the polytropic efficiency is slightly lower than the design efficiency (90 versus 92). This slightly low efficiency is likely within the accuracy of the calculations. The mass flow and calculated total horsepower are also shown. The problem solver concluded that the hypothesis that the compressor required mechanical repairs was not a valid hypothesis. He then considered the question, “would process upsets such as a sudden increase in the recycle gas rate be sufficient to overload the compressor?” He developed a spreadsheet to allow calculation of the horsepower load at various

Table 6-22 Calculated horsepower load versus suction pressure

Variable	Case 1	Case 2	Case 3
LS suction pressure, psig	3	4	5
LS discharge pressure, psig	62	62	62
HS suction pressure, psig	60	60	60
HS discharge pressure, psig	275	275	275
LS suction temperature, °F	100	100	100
LS discharge temperature, °F	283	275	267
HS suction temperature, °F	110	110	110
HS discharge temperature, °F	280	280	280
Compression exponent	0.193	0.193	0.193
Polytropic efficiency	90	90	90
Polytropic head	67400	65900	64500
Mass flow rate, lbs/minute	620	655	690
Total horsepower	1480	1523	1575

low-stage suction pressures. The results of these calculations are shown in Table 6-22.

The problem solver believed that his calculations clearly indicated that the reason for the mysterious compressor shutdowns was associated with a slight increase in process gas rates that caused the compressor suction to increase to the point that the compressor motor was overloaded. This was in spite of intuitive thinking that said the horsepower load should decrease as the compression ratio is decreased. The 1500-BHP motor with a 3 percent overload factor would likely shut down if the compressor suction pressure exceeded 4.5 psig. He expressed his hypothesis as follows:

“It is believed that the mysterious recycle compressor shutdowns are caused by spikes in the recycle gas rate that cause the motor to overload as the suction pressure is increased.”

While it might seem that this hypothesis could be confirmed by a simple analysis of the low-stage suction pressure and compressor amperes versus time, the exact point of shutdown was not obvious. As the compressor suction pressure rose and the compressor shut down, the pressure continued to rise rapidly. It was impossible to determine whether the shutdown occurred when the pressure reached 4, 4.5, 5 or 6 psig.

Step 4: Provide a Mechanism to Test the Hypothesis

The problem solver considered that his best option to test his hypothesis was to run a test at reduced production rates. A test was run at a low enough

production rate that the recycle gas never got high enough to cause the suction pressure to go above 4 psig. During this test, there were no mysterious compressor shutdowns.

Step 5: Recommend Remedial Action to Eliminate the Problem without Creating Another Problem

While this test was successful at preventing the mysterious compressor shutdowns, it was obviously not a permanent solution. Experience with the process over the early start-up period indicated that the recycle gas rate was likely to increase to 15 percent above the steady-state design rate during decreases in reactor conversion. The problem solver looked at an increase in gas rate of 15 percent and concluded that the suction pressure would increase from 3 to 5.7 psig if this occurred. At 5.7 psig, the calculated horsepower load would be 1610 BHP. This would be well above the motor acceptable load with the 3 percent overload factor. He discussed the situation with the motor manufacturer and found out that operating the motor continuously at 10 percent overload would be expected to shorten the life of the motor by a slight amount. Since the 10 percent overload would only occur during times when the reactor conversion dropped, a larger overload switch was installed.

6.20 LESSONS LEARNED

While this problem solution may seem obvious, it should be recognized that the initial assessment was that there was a problem with the “first out” instrumentation system. If this idea had been followed with no thought of other possible hypotheses, there would have been a significant delay in solving the problem since the problem was thought to be an intermittent failure. In addition, while the 3 percent overload rating may seem too conservative, without the calculations done by the problem solver it would not be known whether the 10 percent overload rating would cover the range of loads to be expected. The calculations also helped to steer the problem solver away from the conclusion that there was a mechanical problem with the compressor.

This problem also illustrated that what might seem to be intuitively correct (lowering the compression ratio by increasing the suction pressure will decrease the horsepower load) is not always true. While it is true that lowering the compression ratio by increasing the suction pressure lowers the polytropic head, it also increases the mass flow rate. Both polytropic head and mass flow rate are important in determining the horsepower load. The exact relationship between suction pressure and horsepower load can only be determined by calculations.

Chapter 6 Table of nomenclature

BHP	The energy delivered to the fluid, horsepower
C	The residual gas remaining in the positive displacement compressor clearance pocket or rotating pocket after discharge, fraction of displacement volume
C_p	The fluid-specific heat, BTU/lb-°F
D	The diameter of the pump cylinder, feet
D_p	The diameter of the suction pipe, feet
E	The hydraulic pump efficiency or adiabatic/polytropic compression efficiency, percent
E_T	The turbine efficiency, percent
E_V	The pump or compressor volumetric efficiency, percent
F	The flow rate, lbs/minute
g_c	The gravitational constant
H	The pump head or adiabatic/polytropic head, feet
H_i	The inlet steam enthalpy, BTU/lb
H_o	The outlet steam enthalpy, BTU/lb
H_E	The outlet steam enthalpy with isentropic expansion, BTU/lb
$(h_A)_{MAX}$	The maximum acceleration head loss for a reciprocating pump, feet
K	A factor for reciprocating pumps that depends on the pump design
k	The ratio of specific heats, C_p/C_v
L	The leakage of gas around the piston or rotating element, fraction of displacement volume. It is roughly 2 percent of the compression ratio expressed as a fraction
L_s	The length of the pump stroke, feet
L_p	The <i>actual</i> suction pipe length, feet
LW	The frictional loss in the piping system
M	The gas molecular weight
n	The constant used to define the polytropic compression exponent $\sigma = (n - 1)/n$
P_D	The discharge pressure, psia
P_s	The suction pressure, psia
R	The compression ratio
S	The pump speed, rpm
T_D	The absolute discharge temperature, °R
T_s	The absolute suction temperature, °R
V	The reciprocating pump capacity, ft ³ /minute

V_P	The peak velocity in suction pipe of a reciprocating pump, feet/second
w	The amount of work added by the prime mover
Z	The average (suction and discharge) compressibility
ΔP	The pressure difference between two points or pressure rise across a pump
ΔT_H	The Joule Thompson cooling effect, °R
$\Delta(v^2)$	The difference in velocity squared between two points
Δz	The difference in elevation between two points
ρ	The pumped fluid density, lbs/ft ³
σ	The polytropic or adiabatic compression exponent

APPLICATION TO PLATE PROCESSES

7.1 INTRODUCTION

Examples of plate processes are fractionation towers, extraction towers, absorption towers or any process that depends on mechanical design to provide *intimate contact* between two phases followed by a zone where *phase separation* is achieved. The intimate contacting followed by phase separation allows equilibrium between the two phases to be achieved or approached.

The information provided in this chapter is intended to provide a basis for the problem solver to successfully complete Step 3 of the problem-solving discipline:

“Develop a theoretically sound working hypothesis that explains as many specifications of the problem as possible.”

Since much of what occurs in a plate process is not visible to the naked eye and may not be easily understood by X-rays, it is important to be able to correctly imagine what is occurring inside the equipment.

Fractionation using sieve trays is discussed in this chapter since it is the most common application. However, the principles are applicable to all fractionation tray designs and any other plate processes.

7.2 FRACTIONATION WITH SIEVE TRAYS

The purpose of a sieve tray is to provide as close an approach to equilibrium between the liquid and vapor phase as is reasonably possible. To do this, the following three zones are required:

1. A high intensity vapor–liquid contact zone. In this zone, liquid must be the continuous phase. That is, vapor bubbles must exist as discrete entities surrounded by a liquid phase regime.
2. An entrained liquid separation zone. This vapor continuous zone is immediately above the continuous liquid phase. In this zone, the liquid droplets entrained with the rising vapor disengage and return to the liquid phase.
3. A vapor froth separation zone. The liquid leaving each tray contains vapor that has not yet disengaged from the liquid. The downcomer provides time for disengagement to occur.

Figure 7-1 shows a typical sieve tray illustrating these three zones. In addition, it indicates two other important parameters for a fractionating tray design. These are as follows:

1. The inlet downcomer must be sealed. That is, the head of the clear liquid on the tray must be greater than the clearance between the downcomer and the tray deck. This criterion will force liquid to build up in the downcomer so that the downcomer is sealed. If this criterion is not met, vapor can flow up the downcomer rather than through the holes on the tray above.
2. The hydraulic gradient (the difference in clear liquid height between the inlet downcomer and outlet downcomer) must be minimized. If the hydraulic gradient is too great, the trays will have a tendency to weep liquid on the inlet side of the tray.

Tray stability diagrams provide an analytical means to help visualize what is occurring on a fractionating tray. Figure 7-2 provides an example of a tray stability diagram. The four areas of unacceptable operation are:

1. Flooding—This condition is marked by vapor velocities based on the tower cross-sectional area being so high that large amounts of liquid are carried up into the continuous vapor phase regime. This liquid does not adequately disengage from the vapor and is carried up into the tray above. This condition leads to excessive loading in the tray outlet downcomer as the entrained liquid returns to the tray below via the downcomer. This excessive loading causes the liquid level in the downcomer to build up to an unacceptable level. Flooding tends to start at one tray and propagate upward through a section of the tower. It may often be

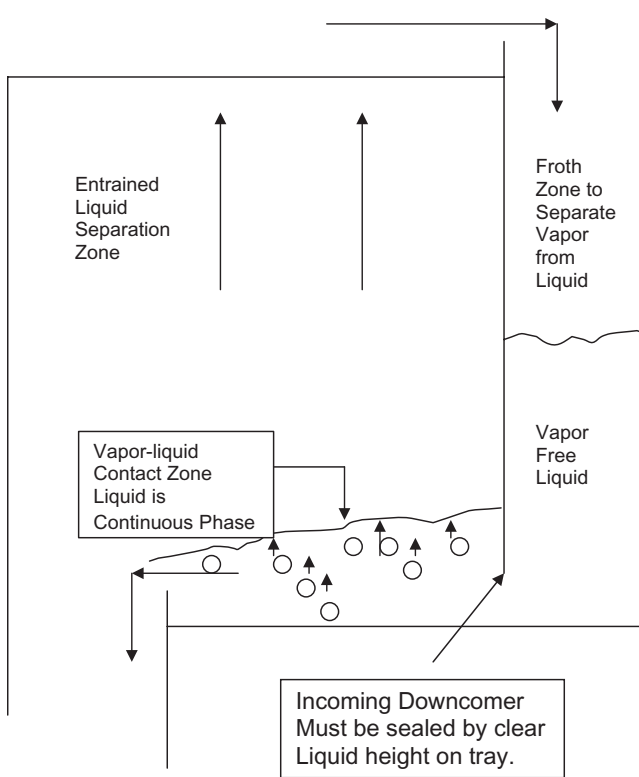


Figure 7-1 Typical fractionation tray.

detected by a measurement of differential pressure across a section of the tower.

2. **Downcomer Filling**—This condition is marked by the downcomer either completely filling or filling to the point that adequate vapor disengagement cannot occur. It can be caused by flooding as indicated earlier or excessive liquid rates. It can also be caused by tray or downcomer restrictions. In a similar fashion to flooding, it can propagate up a fractionating tower.
3. **Blowing**—In this condition, vapor velocity through the holes in a fractionating tray is so high that the vapor phase becomes the continuous phase in the high intensity vapor-liquid contact zone. It is usually caused by a combination of low liquid rates and high vapor rates.
4. **Weeping/Dumping**—In this condition, the vapor rates are so low that liquid pours down the holes in the tray. This results in a very low liquid level on the trays. This usually results in the loss of the downcomer seal causing vapor to flow up the downcomer. This single unsealed downcomer will likely cause a high degree of frothing, which will lead to liquid

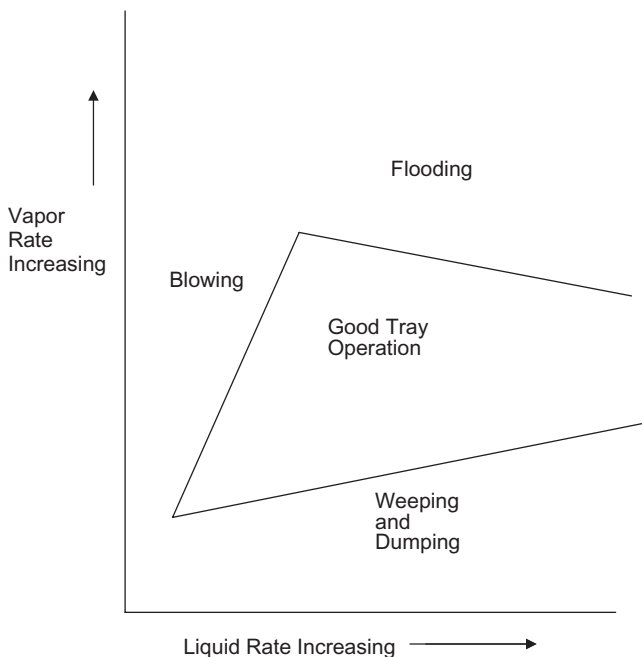


Figure 7-2 Typical tray stability diagram.

holdup in the downcomer. This may result in downcomer flooding in the trays above the tray that is weeping and/or dumping. It should be noted that tray weeping/dumping could also be caused by mechanical damage such as a tray segment that has come loose and is hanging down from its support.

As a general rule, the symptoms of “flooding” and “downcomer filling” are a higher than normal pressure drop across the tower and loss of fractionation. The “blowing” and “weeping/dumping” symptom is loss of fractionation in the tower. Pressure drop for these conditions may be normal or slightly lower than normal.

The tray stability diagram can be developed by the following procedure:

1. Assume a liquid rate.
2. Vary the assumed vapor rate at this assumed liquid rate until the weeping, blowing, flooding or downcomer filling limits are encountered.
3. Repeat this calculation for several different liquid rates until the tray stability diagram can be completed.

The calculation techniques for determining the various tray limitations are beyond the scope of this book. Adequate references are available in the open

literature or in individual company literature. The key point is that a tray stability diagram provides a means to visualize what is happening in the tower and thus will be helpful in Steps 3 through 5 of the disciplined problem-solving approach.

7.3 PROBLEM-SOLVING CONSIDERATIONS FOR FRACTIONATING TOWERS

Assuming that the fractionating tower was designed correctly, problems will almost always be associated with process changes or mechanical damage. Confirmation that the fractionating tower was designed correctly can be done by developing a tray stability diagram. This tray stability diagram will allow plotting operating conditions on the diagram to confirm that they are in the regime of “good operations”. Developing this tray stability diagram is also consistent with the premise of this book—Calculations should be done prior to developing hypotheses that might explain the problems being encountered.

Mechanical damage to trays can create tray performance problems. Some of these possible areas of tray damage or improper tray installations are described in the next few paragraphs.

A tray segment can fail. Most sieve trays are designed to be installed and/or removed through manways that are 18 to 36 inches in diameter. This approach also facilitates tray inspection and replacement. Thus, a single tray will consist of several segments connected together. If one of these connections should fail, a condition similar to weeping/dumping will occur. As indicated earlier, this can propagate upward causing a loss of several theoretical trays.

The trays may not be level. While this is almost always an installation problem, it might also occur after an extended period of operation. This delayed manifestation could be due to extreme foundation settling. In addition, problems associated with uneven trays might not show up under all operating conditions. A tray slope of less than 0.2 percent is generally acceptable and slopes of up to 0.7 percent have provided good operations. Highly critical towers (vacuum towers for example) are special cases.

There may be restrictions in the tray. The presence of solids in a fractionating tower will often lead to plugging of a downcomer or plugging of holes in sieve trays. Solids can be present in the tower due to multiple causes such as:

- Construction debris—It is not unheard of to discover items such as rags, tools or even safety equipment left behind in a tower after construction or repairs. Unfortunately, there have been occasions when an inspection of the tower prior to start-up did not find the debris that blocked a downcomer. Following the start-up of the tower, problems were experienced and a subsequent shutdown and inspection revealed the debris in the downcomer.

- Entrainment from a drum containing solids—Very fine particles can often be entrained from a vapor–liquid disengaging drum and carried into a tower. If these particles are not soluble in the liquid on the trays in the tower, they can accumulate in either the downcomer or sieve tray holes.
- Corrosion of the tower internals—If the liquid on the trays contains a corrosive compound, the trays may begin to corrode. This could cause the holes in the sieve trays to enlarge. In addition, it is possible that some of the corrosion products could be deposited lower in the tower as the composition of the liquid changed. Because of this possibility, sieve trays are often fabricated from a corrosion-resistant material such as stainless steel.
- Reaction of trace components inside the tower—While this would seem like an unlikely event, there have been instances where small quantities of water reacted with a soluble material in the liquid phase on the tower trays and formed an insoluble material. This material would accumulate in the sieve tray holes and the downcomers and create plugging problems in a similar fashion to the item discussed earlier.

The vapor inlet flow pattern may change. For example, the holes in a sieve tray may enlarge or become irregular due to corrosion or the valves in a valve tray may become loose. Either of these may cause significant disturbances to the vapor inlet flow pattern resulting in poor tray performance.

Process changes causing poor tray performance may be due to known changes such as an increase in rates or very subtle changes. For example, there may be instrumentation errors that cause excessive vapor or liquid rates. Even at constant liquid and vapor rates, foaming caused by trace quantities of a surface-active ingredient may occur. An even more subtle change might be the tower that appears to be operating perfectly normal until an event such as described earlier. The presence of water from an exchanger leak reacts with a soluble material to form solids. These solids lead to plugging of the holes in the sieve tray. The first indication of a problem might be the increased differential pressure across the tower.

7.4 DEVELOPMENT OF THEORETICALLY SOUND WORKING HYPOTHESES

Once Step 1 (*Verify* that the problem actually occurred) and Step 2 (*Write* out an accurate specification of the problem) have been completed, the following guidelines can be used to develop a working hypothesis.

Calculations can be performed to determine the following:

- Tray Stability Diagram—This will highlight the areas of unacceptable tray operation, as well as indicating the current point of operation. If the

current operations are in an unacceptable area, this must be corrected before considering any other calculations.

- Number of Theoretical Stages required for the degree of separation being encountered—Knowing the concentrations at various points in the tower, the number of theoretical stages required to make this separation can be estimated by computer or manual techniques. These manual techniques and their place in the modern world are discussed in Chapter 12.
- Estimated tray efficiency—The tray efficiency is the theoretical stages divided by the actual stages and expressed as a percentage. It is a technique to allow estimating the number of actual stages required if the number of theoretical stages is known. While this book does not cover the techniques, there are multiple methods available to estimate the tray efficiency.

It should be noted that these calculations will require good plant data and tower/tray design information. Instrumentation should be calibrated before using plant data to perform these calculations to avoid having to redo the calculations.

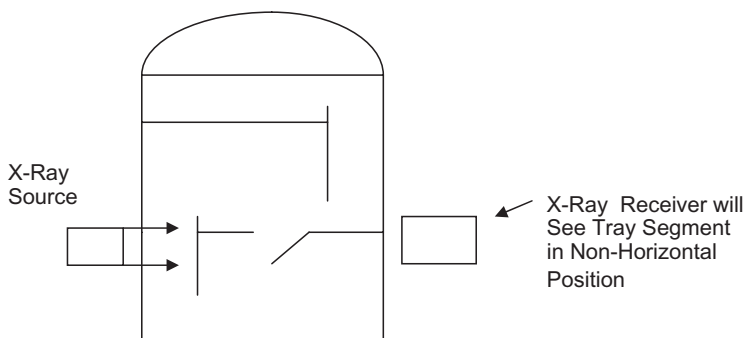
Assuming that the calculations described above indicate that the tower should be performing better than what the actual data indicate, the list of questions given in Chapter 5 can be used to help formulate a working hypothesis. Once a hypothesis is formulated, it may be of value to develop a plant test to confirm the hypothesis. Measurements of tray temperatures, pressures and compositions will be helpful in determining what areas of the tower are worthy of future analysis. Several meaningful approaches are shown in Table 7-1. In addition, X-rays can be utilized to examine the suspect area of the tower to either help formulate a hypothesis or provide a mechanism to test the hypothesis (Step 4: *Provide a mechanism to test the hypothesis*). Some examples of the use of X-rays are shown in Figure 7-3.

7.5 PROBLEM-SOLVING REBOILER CIRCUITS

Reboilers which are often straightforward in the conceptual stage are often a significant part of a plant fractionation problem. The most frequent culprit is the vertical thermosiphon reboiler. A typical flow sheet is shown in Figure 7-4.

Thermosiphon reboiler problems are often due to hydraulics. The operation of this class of reboilers depends on a delicate balance of elevation, fluid densities and pressure drop. The density of the return line to the tower is a function of the percent vaporization. These thermosiphon reboilers almost never operate with pure vapor in the return line to the tower. Thus, the amount of vaporization (percent vaporization) in the reboiler will determine the density in this tower return line. There must be sufficient head to cause

1. Dropped Tray Segment



2. Plugged Downcomer

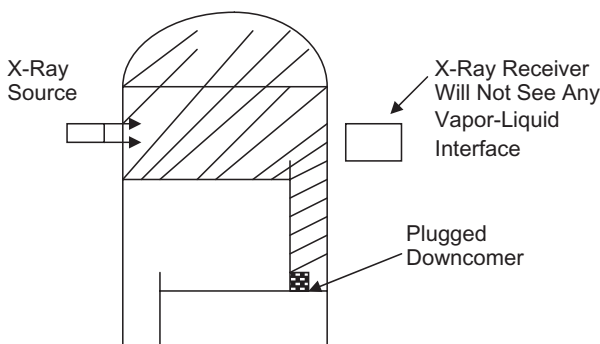
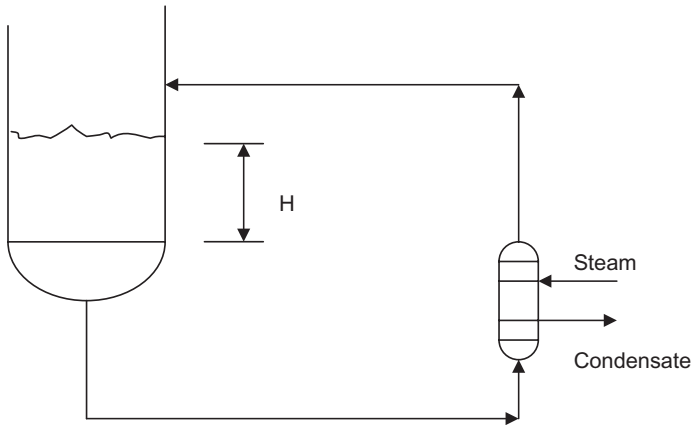


Figure 7-3 Examples of tray problems detectable by X-rays.

the system to circulate with no application of external work. Some of the possible causes of hydraulic problems are described in the following paragraphs.

There may be inadequate head of liquid in the tower bottom. If the liquid level in the bottom of the tower is not high enough, the driving force to cause the process liquid to flow will be inadequate. This may result in a lower than design liquid level in the reboiler and/or a lower than design circulation rate. The low reboiler level will cause the surface area available for vaporization to decrease with a likely loss of heat input to the tower. In addition, if the process liquid flow decreases and the heat input remains the same, the percent vaporization will increase. In some applications, this may create reboiler fouling.

There may be restrictions in the reboiler inlet or outlet piping. This will create additional frictional piping loss. The result of this problem will be



H = Liquid Height that causes reboiler to circulate

Feed to reboiler is all liquid

Vapor return line contains a mixture of liquid and vapor. Typically this line contains 5 to 25 percent vapor. The amount of vapor in this line which is also referred to as the percent of vaporization is set by the pressure drop in the liquid and vapor return line.

Figure 7-4 Thermosiphon reboiler operating principles.

Table 7-1 Evaluation of trays by sampling/data analysis

Measurement	Typical Values	Meaning of Atypical Values
Pressure drop across trays	Should be measured across as few trays as possible Check measurements with calculations Normal values 0.05–0.20 psi/tray. Lower for vacuum towers	Trays plugged, damaged or flooded
Temperature change across trays	Should be equivalent to that estimated from fractionation calc. or equivalent to historical values	Tray damage or process changes
Composition of liquid on trays	Should be equivalent to that estimated from fractionation calc.	Numerous
Venting sample bomb of tray liquid	For pressure towers, vaporizing liquid should cool off bomb	Liquid phase is not present on tray
Composition of vapor on trays	Should be equivalent to that estimated from fractionation calc.	Numerous
Venting sample bomb of tray vapor	No temperature change	Tray flooding

similar to that discussed in the earlier paragraph. That is, the increased circuit pressure drop may result in a lower than design liquid level in the reboiler and/or a lower than design circulation rate.

There may be excessive head in the tower bottoms. A high level in the tower bottom may cause cycles in a reboiler operation. This high level leads to a high circulation rate through the reboiler circuit. This will result in a high fluid density (low percent vaporization) in the reboiler outlet. With the higher fluid density, the circulation rate will decrease. The reduced circulation rate will cause the percent vaporization rate to increase, which will increase the circulation rate. The result of this can be a wildly cyclic operation of the reboiler circuit.

The tower level may be higher than the reboiler return line. While avoiding this seems obvious, the instrumentation sometimes is designed so that what seems to be a reasonable tower level is actually above the reboiler inlet.

If an inadequate reboiler performance is thought to be associated with a hydraulic problem, the best approach to generating a theoretically sound working hypothesis is to either redo or review the original hydraulic calculations. These calculations might be in error or be based on an incorrect length of equivalent piping. It is possible that the actual piping detail is radically different than that assumed by the process designer. This review should also include confirming that the tower elevation relative to the reboiler is the same as in the original design. If the original calculations appear to be correct and consistent with the actual installation and operating details, then it is likely that there is a piping restriction somewhere in the reboiler piping circuit. The more common problem-solving tool of changing the level in the tower without first considering the hydraulic calculations will not be helpful.

Another possible reboiler problem is associated with inadequate drainage of the steam condensate. This will cause a high level of condensate in the reboiler resulting in some of the reboiler surface area being covered with condensate rather than condensing steam. This can also lead to poor stability in the reboiler control circuit. Some of the reasons for poor removal of condensate are described in the following paragraphs.

The steam traps can be improperly sized or can be malfunctioning. If this occurs, condensate will build up in the reboiler until the trap opens to discharge condensate.

Steam pressure modulation control systems often create problems when low-pressure steam is used. If the reboiler is controlled by a control valve in the inlet steam line, it is possible for the pressure on the steam side of the reboiler to be lower than the pressure of the condensate return system. Since the steam pressure in the reboiler is lower than that in the condensate system, the condensate level in the reboiler will increase covering some of the tube area with condensate. As the tube area is covered, the steam pressure must increase to compensate for this. As the steam pressure increases, the conden-

sate is drained from the reboiler. This cycle will be repeated leading to instability in the condensate removal system. This instability in the condensate removal system is often transmitted to the tower.

The temperature driving force needs to be at an optimum level. The temperature difference between the heating medium and process side must not be too great or too small. A large difference (greater than 100 °F) can produce film boiling instead of nucleate boiling. This film boiling causes a vapor film to exist at the tube wall. Under some conditions, this will result in a much lower heat transfer coefficient than design. On the other hand, operating with a close approach between the heating fluid and process fluid can cause the reboiler to surge. That is, the reboiler will cycle between no heat input and greater than design heat input. This surging can be caused by depletion of volatile materials in the reboiler. If low-pressure steam is used on a reboiler that heats a mixture of a volatile material (propane) and nonvolatile material (octane), depletion of the volatile material will cause the reboiler to stop condensing any steam until the inventory of the volatile material is replenished. In addition, the same effect can be observed due to depletion of water from a water–low volatility hydrocarbon two-phase mixture. In a similar fashion to that described above, this will result in a rapid change in boiling point and cause the reboiler to stop condensing steam until the water concentration is replenished.

Solving a reboiler problem can require from almost no engineering to a great deal of engineering problem-solving skills. However, regardless of the technical complexity, the principles of problem solving can still be applied. The questions given in Chapter 5 will still be of value. In addition, simple instruments can be utilized for Step 3 (Develop a *theoretically sound* working hypothesis that explains the problem) and Step 4 (Provide a mechanism to test the hypothesis) of the problem-solving approach. Examples of these instruments are:

- An infrared thermometer can be used to measure the temperature of a suspect steam trap.
- A gauge glass and pressure gauge can be used to measure the condensate level and pressure in a reboiler that is cycling excessively.

More complicated instrumentation might be used as follows:

- A highly sensitive pressure drop instrument might be connected to a high-speed recorder or a process control computer with a rapid scan frequency. This could be used to diagnose reboiler hydraulic problems.
- A device such as a calorimeter that is capable of determining the enthalpy of a process stream could be used to measure the enthalpy of a stream leaving a reboiler. This will allow determination of the percent vaporization that is occurring in the reboiler.

Table 7-2 T-1 operating conditions

	Good Operation	Current Operation
Feed rate, lbs/hr	100000	100000
Feed composition, wt percent C_3	30	40
Feed enthalpy	Saturated liquid	Saturated liquid
Vapor boil-up, lbs/hr	79500	124000
Reflux rate, lbs/hr	31300	65000
Reflux enthalpy	Saturated liquid	Saturated liquid
Distillate comp., wt percent C_3	95	80
Control tray comp., wt percent C_3	60	60
Bottoms, comp., wt percent C_3	2	2

7.6 EXAMPLE PROBLEM 7-1

A propane/butane fractionation tower (T-1) had ceased to operate like it should. The data shown in Table 7-2 represent good and current operation.

A schematic flow diagram is shown in Figure 7-5. In addition to the data shown above, the chronological information shown in the following paragraphs was available.

A routine repair and inspection downtime on the tower occurred sometime after the “good operation” data were recorded. During this downtime, the existing trays which showed evidence of corrosion were removed and new trays with the identical design were installed. While this seemed to go well, the normal mechanical supervisor was off sick during the tray installation procedure. No obvious change in performance was noticed immediately. However, it was several weeks before full rates were achieved due to limited product demand.

The laboratory began using a different gas chromatograph (GC) than was used during the “good operation” period. This GC was thoroughly checked out in a series of cross-checks with the old GC and other laboratory GCs. One of the laboratory technicians that had analyzed this sample for 10 years was reporting that he finds a film of heavy hydrocarbons or oils in the GC after each analytical run. All flowmeters and temperature instruments had been confirmed to be accurate.

When the problem solver was assigned the problem, he began by using the five-step procedure discussed earlier. He combined Steps 1 and 2 as follows.

Step 1: Verify that the Problem Actually Occurred

Since all indications were that there was a real problem, the problem solver simply combined the verification with the problem statement given in Step 2.

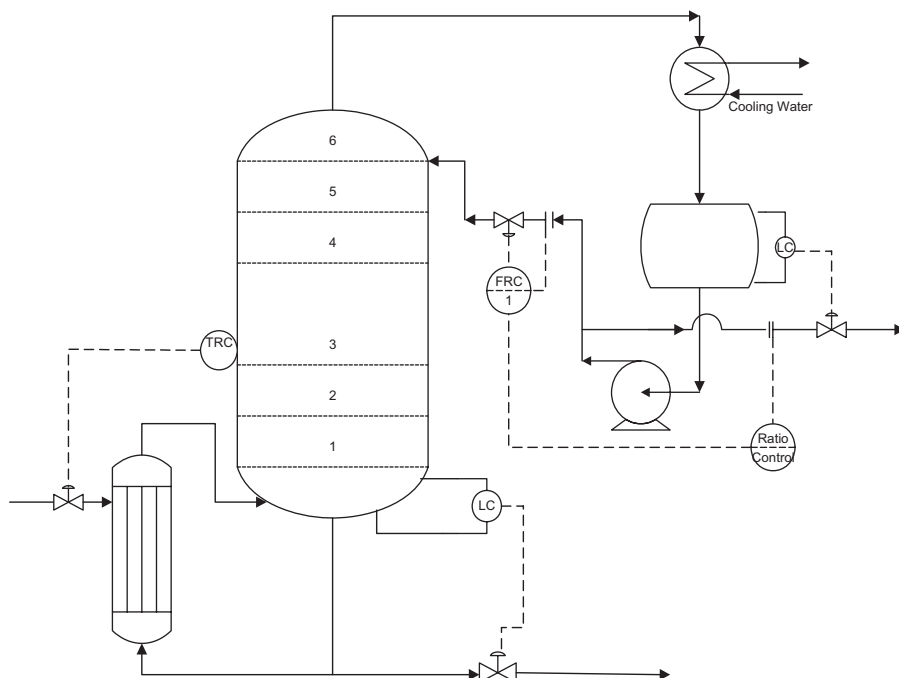


Figure 7-5 Schematic flow for Problem 7-1.

Step 2: Write Out an Accurate Statement of What Problem You Are Trying to Solve

The problem statement that he developed was as follows:

“Currently T-1, the plant Propane/Butane Splitter, is operating poorly based on historical standards. The current plant data indicates that the rectification section is not performing well even though the reflux rate is well above that required for good performance. There were several changes made recently. These changes consisted of new trays, a new GC, and a feed composition change. All of these occurred prior to observation of the loss of fractionation. The loss of fractionation was not noticed until the product demand increased so that the tower began operating at design rates. Determine the reason for the poor performance of the rectification section of T-1.”

Step 3: Develop a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible

When the chronological history was reviewed, it was tempting to believe that the trays were installed wrong. While this was a strong possibility, it did not represent a theoretically sound working hypothesis without adequate

Table 7-3 Questions/comments for Problem 7-1

Question	Comment
Are all operating directives and operating procedures being followed?	No. Operating conditions appeared to be well outside the normal targets.
Are all instruments correct?	All instruments had been calibrated.
Are laboratory results correct?	The new GC had been thoroughly calibrated.
Were there any errors made in the original design?	Not applicable since no design changes were made.
Were there changes in the operating conditions?	Yes. In addition to the known changes, it is possible that whatever caused the percent C3 in the feed to increase might have also caused an extraneous component to be introduced into the tower.
Is fluid leakage occurring?	Damaged trays might cause internal tray leakage which might explain the problem.
Has there been mechanical wear that might explain the problem?	No.
Is the reaction rate as anticipated?	Not applicable.
Are there adverse reactions occurring?	Not applicable.
Were there errors made in the construction?	Maybe. The tray installation might not have been correct.

calculations and additional analysis. The questions in Chapter 5 were utilized along with a tray stability diagram to formulate hypotheses. (See Table 7-3)

While this series of questions did not provide an exact diagnosis of the problem, it was apparent that the tower was operating well beyond the region of experience and operating directives. The first question that the problem solver sought to answer was “Do the current operating rates of the tower variables by themselves explain the poor tray performance?” Two types of calculations using the data were made to allow answering this question.

A tray stability diagram was developed. This is shown in Figure 7-6. This diagram indicates that the top part of the tower is being overloaded and probably is operating in a flooded condition.

The internal tower vapor rate was calculated by material balance and heat balance. These calculated rates were then compared. If flooding was occurring, the vapor rate as determined by material balance would be higher than that determined by an overall heat balance. This is because as the tower floods, liquid would be carried over with vapor from the top tray into the reflux condenser. The total vapor (including entrained liquid) going into the condenser and accumulator would be greater than that estimated from a heat balance on the tower. Regardless of what control scheme was being used, this excess

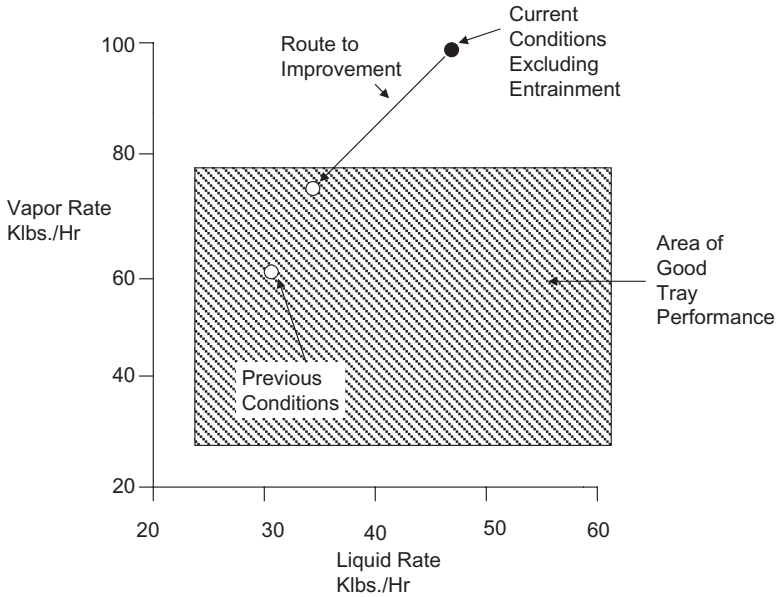


Figure 7-6 Tray stability diagram for Problem 7-1.

liquid must be pumped back to the tower and would show on the reflux flowmeter.

The problem solver calculated the vapor and liquid loading in the top of the tower by material balance and heat balance as follows:

1. He calculated the distillate rate by material balance:

$$F = B + D \quad (7-1)$$

$$F \cdot X_F = B \cdot X_B + D \cdot X_D \quad (7-2)$$

Where:

- F = feed rate, lbs/hr
- B = bottoms rate, lbs/hr
- D = distillate rate, lbs/hr
- X_F = feed concentration, wt percent
- X_B = bottoms concentration, wt percent
- X_D = distillate concentration, wt percent

For the two cases given in Table 7-2, the calculated results are shown in Table 7-4.

Table 7-4 Estimated material balance rates

	Past Operation	Current Operation
Distillate (D), lbs/hr	30100	48700
Bottoms (B), lbs/hr	69900	51300

Table 7-5 Estimated vapor and liquid rates in top of tower

	Past Operation	Current Operation
Liquid (L), lbs/hr	31300	65000
Vapor (V), lbs/hr	61400	113700

Table 7-6 Top vapor rate based on heat input to bottom

	Past Operation	Current Operation
Vapor rate bottom, lbs/hr	79500	124000
Molecular wt, top	44.54	46.23
Molecular wt, btm	57.63	57.63
Vapor rate top, lbs/hr	61400	99500

2. He estimated the vapor and liquid loading in the top of the tower. Since the reflux is not subcooled, the liquid rate (L) in the top of the tower is simply the reflux. In addition, the vapor rate (V) in the top of the tower can be estimated as follows and shown in Table 7-5.

$$V = L + D \quad (7-3)$$

3. Using the principle of “equal molal overflow”, he calculated the top vapor rate (V) based on the heat input to the reboiler. The “equal molal overflow” principle states that for systems with minimal nonideality, the vapor rate throughout the tower expressed in mols/hr is equal, as long as no other vapor or heat input is introduced. The tower feed is a saturated liquid; therefore, there is no other vapor generated when the feed is added to the tower. In addition, there is no other heat input to the tower. Thus, the equation below was used to estimate the vapor rate at the top of the tower from the heat input to the bottom of the tower. The results of this calculation for past and current operations are shown in Table 7-6.

$$V_T = V_B * M_T / M_B \quad (7-4)$$

Table 7-7 Vapor rates calculated from material balances and heat balances

Calculation method	Past Operation	Current Operation
Top material balance, lbs/hr	61400	113700
Bottom heat balance, lbs/hr	61400	99500
Comments	Good check	Poor check

Where:

V_T = vapor rate at the top of the tower, lbs/hr

V_B = vapor rate at the bottom of the tower, lbs/hr

M_T = molecular weight of vapor top of the tower

M_B = molecular weight of vapor bottom of tower

The problem solver compared the top vapor rate as estimated from the overhead material balance and from the bottoms vapor rate and developed Table 7-7.

The problem solver now had two independent calculations that indicated that the tower was flooding. The tray stability diagram indicated that the tower was operating in the flooding regime. In addition, the comparison of the heat balances and material balances indicated that there was more material leaving the top of the tower than could be accounted for by a heat balance. The fact that previously this approach gave a good comparison was proof that there was a significant change in the operation of the tower. The problem solver then developed the following hypothesis.

“The poor performance of T-1 is due to flooding of the rectification section that is being caused by the excessive vapor and liquid loading. This excessive vapor and liquid loading might be caused by one of the following:

- Operator error—The reboiler steam rate or tower reflux rate was set too high by operator error.
- Tray installation error—There may have been an error in the tray installation which resulted in poor fractionation and caused the control system or operator to increase the tray loadings to attempt to compensate for this. This caused the tower to operate in a flooded regime.
- Foaming—The presence of a surface-active material might have caused the tower to originally function poorly which then caused a manual or automatic intervention to compensate for this uncovered problem. This intervention caused the tower to begin to operate in a flooded regime.
- Other—There may be other as yet undiscovered explanations for the changes which moved the tower operation into the flooding regime.”

Note that in this problem hypothesis, the problem solver expressed the need to explore what may have caused the excessive tower loadings rather

than to just assume that it was due to an operator or control system error. It should also be noted that while the increased C3 concentration in the feed to the tower is unlikely to be the root cause of the problem, it did indicate that the source of the C3/C4 liquid might have changed. This new source might have resulted in a different trace impurity or an increase in the concentration of an existing trace impurity that would cause foaming in the tower. The possible trace impurities in a C3/C4 liquid stream could include materials used for deicing exchangers (methanol), materials used for removing water (glycol) or materials used for neutralizing acidic compounds (amines).

Step 4: Provide a Mechanism to Test the Hypothesis

The problem solver decided to test the hypothesis by reducing the tray loadings to safe levels as indicated by the tray stability diagram. If this test returned the operation to “past operation” levels, then the mechanism to test the hypothesis becomes a partial solution.

He also considered what would happen if the operation did not return to the conditions and results previously experienced when the tray loadings were reduced. If that contingency occurred, he believed that additional tests or investigation would be required. These additional tests would include one or more of the following:

- Perform more detailed testing using some of techniques shown in Table 7-1.
- Conduct some sort of foaming test. This would probably require some type of pressure-rated laboratory equipment with a sight glass.
- Take X-rays of the appropriate parts of the tower to determine if tray damage is obvious.
- Determine if there has been a change in the source of the C3/C4 liquid and if there was any information on the trace impurities that might be present in this source.

If the reduction of the tray loadings does not solve the problem, it is likely that an expedient solution of reducing the feed rate to the tower may be required to insure producing an overhead product that meets the specifications. However, this is not the solution to the problem, but only a “stop-gap” approach to allow making on-specification product.

Step 5: Recommend Remedial Action to Eliminate the Problem without Creating Another Problem

The actual recommendation for remedial action will depend on the results of Step 4. If reducing the tray loadings does not solve the problem, then the other tests listed in Step 4 must be executed and carefully analyzed to determine the required remedial action.

If reducing the tray loadings does solve the problem, it should be recognized that the basic questions outlined in Step 3 still remain. It is unlikely that improper tray installation would be a transient problem. It is also unlikely that an operator purposefully set the ratio controller outside the range of standard operations without a reason. Thus, the most logical possibility is that there was a transient condition that was due to the presence of a trace impurity or due to some other external event. When the operator encountered this external transient event, he tried to respond to the unmeasured and unknown disturbance by increasing the ratio controller, which caused the tower to begin flooding. Since this transient condition might well reoccur, the tower should be monitored daily to determine when the problem reoccurs. It will be of value to be proactive and plan what analyses or actions will be taken when daily monitoring indicates that the transient condition is returning.

The test of reducing the reflux rate so that the operations were in the good tray operating region was successful in returning the operations to normal rates and purities. A review of the possibility that the sources of the C3/C4 liquid had changed indicated that the source had changed, but since the problem only occurred as the production rate increased, it was impossible to connect this change with the change in tower operation.

As indicated earlier, in this circumstance it is necessary to monitor the tower closely and develop a contingency plan to allow response to the likely return of the transient condition. The problem solver took the following actions:

- He developed a fractionation index, which allowed him to follow the operation of the tower on an hour-by-hour basis.
- He developed a list of samples that were to be obtained the next time that the fractionation index dropped below a specified value.
- He worked with the laboratory to develop new analytical techniques for the bomb samples to allow determining if there were surfactants present in any of these samples. The analytical techniques and GCs used for volatile hydrocarbons would likely not be sensitive enough for very low concentrations of surfactants.
- He developed a foaming test that would be used in case of a significant decrease in the fractionation index.
- He collected the specified samples and used the new analytical techniques to determine the possible presence and concentrations of surfactants in the base case with good operations. He also tested the foaming test on these samples.

7.7 LESSONS LEARNED

While this problem is a fictitious example, it has many elements of real-life problem solving. The multiple events occurring at the same time that make

isolating a single root cause difficult, is a real-life element. The presence and subsequent disappearance of a trace impurity that leads to an unsuspected problem is also a real-life event. There are lessons to be learned from this semi-fictitious example.

There was great value in doing calculations to prove that the tower was flooding. The tray loading diagram was a useful tool for problem solving and also in selling the problem solution to management.

It should be recognized that if daily monitoring had been utilized that the problem would have been spotted immediately as opposed to having to wait until demand increased to the point of requiring the tower to operate at full capacity. While this may seem like an isolated occurrence, many industrial problems lie dormant until it is necessary to increase rates. Also note that it is never too late to begin a daily monitoring system.

This problem also illustrates that there will be occasions when the exact root cause of the problem cannot be determined. In these instances, the problem solver should develop a system that will be effective in collecting data when the next occurrence of the event happens.

While it could be argued that all problems have an obvious root cause, it should be realized that multiple events that may seem to be related to the problem do occur. Thus, the multiple events (mechanical supervisor being sick, new GC, possible change in source of C3/C4 feed, and oil in the GC) for this problem are often typical of industrial problem solving. The problem solver must not discard any set of data or observations, but rather must incorporate them in his problem statement or problem analysis.

Chapter 7 Table of nomenclature

B	Bottoms rate, lbs/hr
D	Distillate rate, lbs/hr
F	Feed rate, lbs/hr
M_T	Molecular weight of vapor top of the tower
V_T	Vapor rate at the top of the tower, lbs/hr
V_B	Vapor rate at the bottom of the tower, lbs/hr
X_F	Feed concentration, wt percent
X_B	Bottoms concentration, wt percent
X_D	Distillate concentration, wt percent
M_B	Molecular weight of vapor bottom of tower

APPLICATION TO KINETICALLY LIMITED PROCESSES

8.1 INTRODUCTION

A kinetically limited process is one that does not go to completion because it is limited by the speed of mass or heat transfer. Completion can be defined as equilibrium or a state that would be reached if an infinite amount of time were available. Examples of this process are heat exchange, reaction and diffusion-limited operations.

The purpose of this chapter is to illustrate how the five-step approach to problem solving can be used to solve problems in this type of process. The chapter shows how a generalized approach can be used to develop theoretically sound working hypotheses for any kinetically limited process. The emphasis is on utilizing this approach in an industrial setting. Thus, the more theoretical approach of using multiple constants has been replaced with an empirical “lumped parameter” approach. A specific example of this that most process engineers are familiar with is the use of an overall heat transfer coefficient rather than individual film coefficients. The overall heat transfer coefficient can be determined from vendor specification sheets or from plant test data when the exchanger is known to be clean.

8.2 KINETICALLY LIMITED MODELS

Any kinetically limited process can be described by the generalized equation (8-1):

$$R = C * DF \quad (8-1)$$

Where:

R = the rate of change with time of the variable under study

C = a constant referred to as the “lumped parameter constant”

DF = the driving force or incentive for mass/heat transfer to occur

For a kinetically limited process, the lumped parameter constant “C” can be used for problem solving in multiple ways. The value of “C” can be determined on an hourly or daily basis and monitored as part of a daily monitoring system. Changes in “C” will be trigger points to start active problem solving. In addition, based on an estimated value of “C”, studies can be conducted to estimate what impact changes in the driving force will have on the rate. This may allow process conditions to be modified to compensate for changes in “C”.

As indicated earlier, the heat transfer relationship shown below is the best-known example of equation (8-1).

$$Q = U * A * \ln \Delta T \quad (8-2)$$

Where:

Q = R = rate of heat transfer

U*A = C = the lumped parameter or for heat transfer, the heat transfer coefficient multiplied by the area

$\ln \Delta T = DF$ = the driving force or for heat transfer, the log mean temperature difference

A more complicated form of equation (8-1) is encountered for reaction and diffusion-limited drying. The driving force in these cases is often related to the concentration of a molecule or the difference between the concentration and equilibrium concentration. For example, for diffusion-limited drying, equation (8-1) becomes:

$$dX/dt = K * (X - X_e) \quad (8-3)$$

Where:

dX/dt = the rate of removal of solvent from a polymer

K = the lumped parameter constant which is somewhat related to diffusion. Since it deals with mass transfer, it is also referenced in this chapter as a mass transfer coefficient

$X - X_e$ = the driving force

X = the actual concentration of solvent in a polymer

X_e = the equilibrium concentration of solvent in the polymer at the same point in time

For a simple reaction between two components where the reaction rate is first order, equation (8-1) becomes:

$$dX/dt = C_R * X * Y \quad (8-4)$$

Where:

dX/dt = the rate of disappearance of component X

C_R = the lumped parameter constant (reaction rate constant)

X = the concentration of component X

Y = the concentration of component Y

Relationships for other kinetically limited processes can be developed starting with equation (8-1). The key to using this equation for developing theoretically sound working hypotheses is the correct selection of the driving force and use of the "lumped parameter" constant.

The need to select the correct driving force can be illustrated by equation (8-3). The correct driving force is the difference between the actual and equilibrium concentration. If the equilibrium concentration is ignored, the constant determined from plant operating data will be lower than actual. Another example where the use of the incorrect driving force will give improper constants is estimation of heat transfer constants in a fuel-fired furnace. Heat transfer from the flames and refractory surfaces to the metal tubes (primarily radiant heat) depends on the driving force for radiant heat transfer rather than convective heat transfer. Where the driving force for convective heat transfer is simply the log temperature difference, the driving force for radiant heat transfer is expressed as shown below:

$$DF_R = T_g^4 - T_m^4 \quad (8-5)$$

Where:

DF_R = driving force for radiant heat transfer

T_g = absolute temperature of gas

T_m = absolute temperature of tube metal

Lumped constant parameters that are developed from plant data will be risky to use for large extrapolations. A lumped parameter constant that can be developed from fundamentals will always have a broader range of applicability. These constants that are developed from fundamentals can be used regardless of how close the operating conditions approach those under which the constant was determined.

However, some constants can be determined from fundamentals only by such an elaborate procedure that it becomes impractical for plant problem-solving activities. For example in diffusion-related drying (equation (8-3)), the lumped parameter constant or mass transfer coefficient depends on the diffusion rate through the polymer, the effective length of the flow path through the polymer particle, the actual particle surface area and the mass transfer coefficients from the polymer surface to the bulk of the gas. Most polymer particles are irregular shaped and have a large number of internal pores. This makes determining items such as particle surface area and flow path through the particle difficult if not impossible to determine. If only one of these individual variables is not available and cannot be developed or determined, then utilizing a lumped parameter empirical constant (overall mass transfer coefficient) provides the only means to evaluate diffusion-related drying. This overall mass transfer coefficient can be determined from plant data, from pilot plant tests or from bench scale tests.

8.3 LIMITATIONS TO THE LUMPED PARAMETER APPROACH

The lumped parameter approach has sometimes been referred to as a “black box” approach. This implies that the person using this approach does not understand the details of what is occurring inside the “black box”. For example, the use of an overall heat transfer coefficient does not take into account the individual film side coefficients, metal resistance and fouling factors. However, in most process plant problem-solving activities, the significant observation is the change in the overall heat transfer coefficient. Whether the decrease of heat transfer coefficient is due to the tube or shell side film coefficient decrease can usually be determined based on experience. For example, the decrease in overall heat transfer coefficient for a fractionating tower overhead condenser that utilizes cooling tower water is almost always due to fouling on the cooling water side. Similar logic would apply to the use of the lumped parameter approach for problem solving other kinetically limited processes.

The limitation of this approach is more severe when designing new facilities based on a lumped parameter coefficient determined from an operating plant. If a more fundamental analysis is not done, the lumped parameter approach can lead to design errors. An example of this is the design of a specialized vertical condenser for a new plant based on a condenser in identical service in an existing plant. The condensation in this vertical condenser took place on the shell side and cooling water was utilized in the tubes. The new plant had slightly higher capacity. To evaluate the overall heat transfer coefficient from pure fundamentals would have required an elaborate model that involved condensate thickness at various points in the vertical exchanger, as well as the traditional resistances such as water side coefficient, condensing side coefficient and metal resistance. Rather than doing this highly theoretical analysis, the design team choose to utilize the overall heat transfer coefficient experi-

enced in the existing plant. However, based on the desire to minimize the overall height of the structure in the new plant, the height to diameter (H/D) ratio of the vertical condenser was reduced. In order to compensate for this reduced H/D ratio, the tube diameter and exchanger shell diameter were increased. No consideration was given to the effect of these increased diameters on the overall heat transfer coefficient. When the unit was started up, it was noticed that the heat transfer coefficient was 20 percent below anticipated values. This underscores the need for geometric similarity when basing a design on empirically developed constants.

In spite of the limitations, when considering plant-related problem solving, the utilization of an empirically derived lumped parameter constant, along with a theoretically correct driving force, is almost always adequate because of the three reasons given below:

1. Daily monitoring of the process requires only an empirical constant.
2. Time is always critical. Laboratory or elaborate investigations to develop fundamental data are rarely appropriate.
3. If it is desirable to make operating changes, the new conditions are generally not a large extrapolation from current conditions. Thus, there is minimal danger of extrapolation.

8.4 GUIDELINES FOR UTILIZATION OF THIS APPROACH FOR PLANT PROBLEM SOLVING

Utilizing the “lumped parameter constant” approach for monitoring and solving plant problems is a powerful tool. However, like all tools it must be used in an appropriate fashion. Some guidelines for using this tool are as follows:

1. Develop a meaningful driving force that is theoretically correct. *It should be noted that there is often a difference between a driving force that appears logical and one that is theoretically correct.* Logic cannot be substituted for the utilization of sound engineering fundamental knowledge. Without a meaningful driving force, the empirically developed lumped parameter constant will not be valid over any range of data.
2. Monitor this lumped parameter constant on a daily basis and over as wide a variety of conditions as possible. If the constant varies, look for correlations between the constant and *independent* variables that make theoretical sense. For example, a correlation between the lumped parameter constant in a diffusion-limited drying process and gas rates makes good theoretical sense. The increased gas rate should increase the rate of mass transfer. If a lumped parameter constant varies with no process changes, it is an indication that an extraneous factor has caused a process

deviation. If this extraneous factor can be eliminated, then the constant should return to normal. If this factor cannot be discovered or eliminated, then process changes will be required.

3. If it appears desirable to recommend a change in the driving force to increase the kinetically limited rate, minimize the length of the extrapolation that uses an empirically developed lumped parameter constant.

8.5 EXAMPLE PROBLEM 8-1

A polymer plant was experiencing problems in stripping the residual solvent from the polymer product. A counterflow agitated dryer with pure nitrogen sweep gas was utilized to strip the solvent. All operating conditions appeared to be normal. In addition, all instruments were checked and appeared to be accurate. A timeline indicated that the problem seemed to begin when a new catalyst was introduced into the process for a plant test. Even though using the new catalyst was considered a test run, it was mandatory that the plant be switched to this new catalyst as soon as possible. One of the key advantages of the new catalyst was the higher bulk density product that could be produced with the catalyst. This had been well demonstrated in pilot plant studies. No drying studies had been conducted in the pilot plant. Drying capability was thought to be associated with sweep gas rate, residence time and temperatures which were not changed when the plant was switched to the new catalyst.

The problem solver was asked to determine what could be done to reduce the solvent levels to the previous concentrations while continuing to operate with the new catalyst. Operating conditions were as follows in Table 8-1.

In addition to the plant data shown, laboratory results indicated that the equilibrium relationships for polymers produced with the old and new catalysts were identical and could be expressed as shown below:

$$X_E = 295000 * (P/VP)^{1.5} \quad (8-6)$$

Table 8-1 Operating conditions with old and new catalyst

	Old Catalyst	New Catalyst
Polymer rate, lbs/hr	20000	20000
Polymer density, lbs/ft ³	25	28
Pure nitrogen sweep gas rate, lbs/hr	1000	1000
Dryer temperature (isothermal), °F	200	200
Hexane vapor pressure, psia	28.7	28.7
Dryer pressure, psia	15	15
Inlet hexane content, ppm	1000	1000
Outlet hexane content, ppm	25	75

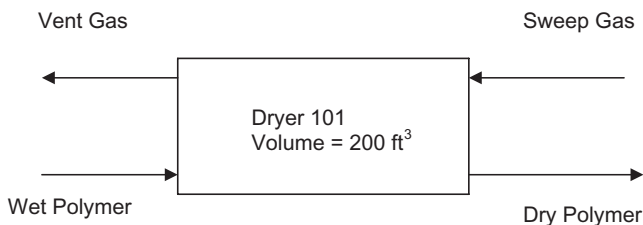


Figure 8-1 Schematic sketch of dryer.

Where:

X_E = the equilibrium concentration of solvent in polymer

P = the partial pressure of the solvent in the vapor phase

VP = the vapor pressure of the solvent at the dryer temperature

A schematic sketch of the dryer is shown in Figure 8-1.

The problem solver began working on the problem by using the five-step problem-solving approach. There was minimal need to verify that the problem had actually occurred. However, he did not skip this step.

Step 1: Verify that the Problem Actually Occurred

The problem solver confirmed that all of the meters were correct and that the hexane content was indeed three times the normal levels.

Step 2: Write Out an Accurate Statement of What Problem You Are Trying to Solve

He wrote out the following problem statement:

“The polymer leaving Dryer-101 contains excessive amounts of solvent. This condition started soon after the introduction of a new catalyst in the polymerization reactors. All operating conditions are normal and the instrumentation is correct. It is desirable to convert the plant to using this catalyst as soon as possible. Determine what operating condition changes or what new equipment is required to achieve 25 ppm hexane in the final product at the normal polymer production rate.”

Step 3: Develop a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible

Referring back to the list of questions given in Chapter 5 was helpful in formulating possible hypotheses. The problem solver reviewed these questions and formulated appropriate comments for this example problem as shown in Table 8-2.

Table 8-2 Questions/comments for Problem 8-1

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed.
Are all instruments correct?	The instruments had allegedly been calibrated.
Are laboratory results correct?	Yes.
Were there any errors made in the original design?	Not applicable.
Were there changes in operating conditions?	New catalyst was started.
Is fluid leakage occurring?	Not applicable.
Has there been mechanical wear that would explain the problem?	Not applicable.
Is the reaction rate as anticipated?	The new catalyst might cause the polymer particles to be less porous. This would cause a lower than anticipated "mass transfer coefficient".
Are there adverse reactions occurring?	See above.
Were there errors made in the construction?	Not applicable.

As might be expected, these questions pointed strongly to the idea that the problem began when the new catalyst was introduced to the process. They also provided some possible explanation for why the new catalyst would cause a drying problem to occur. It was theorized that the new catalyst created a less porous particle. The lower porosity would cause the diffusion of the solvent through the particle to be slower. This less porous particle would also have a higher particle density, which would explain the higher bulk density. It should be noted that if this list of questions was not utilized, the change in catalyst would have been pinpointed as the cause, but the explanation of the formation of a less porous polymer particle might have been missed.

As indicated in equation (8-3), the relationship between rate of drying and driving force for a diffusion-limited drying process can be expressed as follows:

$$dX/dt = K*(X - X_e) \quad (8-3)$$

Since the problem statement indicates that all operating conditions were normal and laboratory results indicated that the equilibrium relationship for both catalysts was the same, there must be a difference in the "K" values between the two catalysts.

While a working hypothesis that the "K" value has changed is a perfectly valid hypothesis, it does not help determine what the next step should be

because it does not specify the magnitude of the change. If the magnitude of the change is not known, it will be impossible to determine if operational changes or addition of new equipment will be required to allow operation with the new catalyst. Thus, the theoretically sound working hypothesis must include an estimate of the magnitude of the change in the mass transfer coefficient ("K" value).

The value of "K" can be estimated by simple integration if X_e (the equilibrium concentration of solvent in the polymer) is equal to zero. In this special case, integration yields the following:

$$X_f/X_o = e^{-Kt} \quad (8-7)$$

Where:

- X_f = the concentration of solvent in the outlet polymer
- X_o = the concentration of solvent in the inlet polymer
- K = the rate constant or mass transfer coefficient, 1/minutes
- t = the amount of time in the dryer, minutes

For the general case where X_e is not equal to zero, numerical integration must be used to determine the unknown variable. This numerical integration can be used to determine the mass transfer coefficient (K) or the outlet concentration of solvent in the polymer (X_f). This numerical integration can be developed by visualizing a dryer segment as shown in Figure 8-2.

The equilibrium concentration in Figure 8-2 can be determined by a Henry's Law type relationship as shown below:

$$X_e = C_E * Y \quad (8-8)$$

Where:

- C_E = a constant determined from experimental data or application of theoretical principles
- Y = the vapor phase composition at any point in the dryer

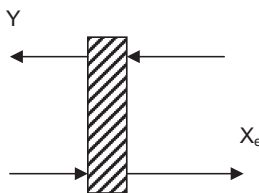


Figure 8-2 Dryer calculation segment.

For the example problem, the equilibrium relationship shown in equation (8-6) can be utilized in place of that shown in equation (8-8) to determine the equilibrium concentration based on the vapor phase concentration.

The integration of equation (8-3) when X_e is not equal to zero, yields the following:

$$\int dX/(X - X_e) = Kt \quad (8-9)$$

For this problem, it is desired to obtain the “K” value for each catalyst system. To determine the “K” value from this relationship using numerical integration requires the following steps using the data given above and a spreadsheet:

1. Use values of the polymer and gas rates, along with the inlet and outlet hexane concentrations in the polymer, to determine the concentration of hexane in the outlet gas. Note that the data indicated that pure nitrogen was used as the sweep gas.
2. Calculate the total residence time in the dryer assuming no “back-mixing”. This can be calculated by dividing the polymer holdup in the dryer by the polymer rate.
3. Split the dryer into several segments (100 to 500) and calculate the dx for each segment. The change in the volatiles concentration (dx) will simply be the total change in volatiles concentration divided by the number of dryer segments. The time increment (dt) can be determined in a similar fashion.
4. From the relationship given in equation (8-6) and the outlet vapor composition, calculate the X_e of the polymer leaving the first segment.
5. Since this segment represents only an exceptionally small part of the dryer, the actual solvent concentration (X) can be considered constant throughout this segment. For this small segment:

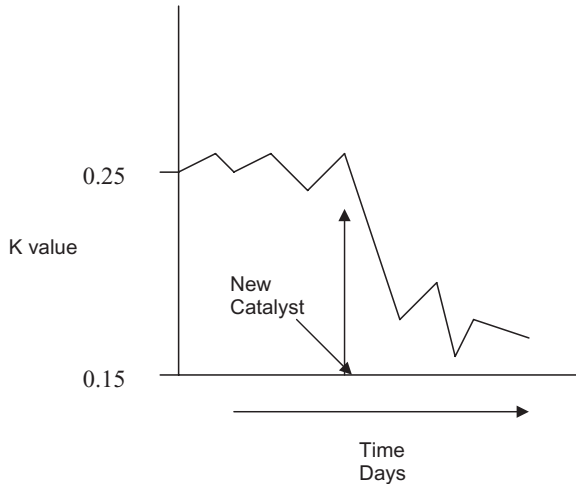
$$(Kdt)_i = dX/(X - X_e) \quad (8-10)$$

In equation (8-10), the term $(Kdt)_i$ is simply the product of the lumped parameter drying constant (mass transfer coefficient) and the residence time in the small segment. The lumped parameter drying constant is assumed to be the same in all segments.

6. Using dx , the gas and polymer rates and the gas concentration leaving the first segment, calculate the gas concentration entering the segment by a material balance around the segment. This will be the gas concentration leaving the next segment.

Table 8-3 Results of numerical integration

Catalyst	K Value, 1/minute
Old	0.25
New	0.16

**Figure 8-3** K value versus time.

7. Continue this process until the same calculations have been made for each segment. Then “K” can be calculated as follows:

$$K = \xi(Kt)_i/t \quad (8-11)$$

When the problem solver performed these calculations for the two cases described earlier, the following values of “K” were obtained as shown in Table 8-3.

Extensive data were available from computer archives so that the value of “K” over the period of interest could be evaluated. When this was done, Figure 8-3 clearly showed that the mass transfer coefficient decreased when the new catalyst was introduced into the system.

A theoretically sound working hypothesis that fits the data would be:

“The recent loss of drying capability is associated with a decrease in the mass transfer coefficient (K) that occurred when the change to the new catalyst occurred. It is believed that this change is due to the lower porosity of the polymer particle produced with this catalyst. Evidence that supports this is the 35 percent lower “K” value and the higher bulk density.”

Step 4: Provide a Mechanism to Test the Hypothesis

At this point, the problem solver gave consideration to the question of “optimum technical depth”. Several alternatives were available to test the hypothesis. The optimum alternative depended on the cost of the solution, the confidence level required and the cost of continuing poor drying performance. In this polymer process, the customer specifications and/or needs were considered more important than operating at full capacity. Thus in this case, the cost of the poor drying performance was the lost profits associated with operating at lower than design production rates. Alternatives for testing the hypothesis that were considered were:

- Conducting a test run using the old catalyst to confirm that the old catalyst really had a “K” value higher than the new catalyst.
- Using the “K” value for the new catalyst to estimate what changes in operating conditions would be required to reduce the hexane concentration from 75 to 25 ppm.
- Modifying the new catalyst so that it produced a polymer similar to the old catalyst.

In order to determine if operating conditions could be modified to reduce the hexane to 25 ppm, the problem solver made calculations using the approach described earlier. However, in these calculations, the “K” value was known to be 0.161/minutes. The value to be estimated was the outlet solvent concentration. The same spreadsheet and approach were used. The problem solver changed the operating variables as desired and then varied the outlet solvent concentration in the polymer until the calculations based on the spreadsheet indicated a “K” value of 0.161/minutes. Based on the calculations, he concluded that increasing the sweep gas by a factor of 10 (1000 to 10000 lbs/hr) would reduce the hexane content from 75 to 65 ppm. This was obviously not a valid approach. The calculations also indicated that if the residence time in the dryer were increased from 17 to 24 minutes, the hexane concentration would be reduced to 25 ppm. This could be accomplished in a plant test by reducing the polymer production rate to 14000 lbs/hr. The volumetric holdup in the dryer was constant so that the only way to increase residence time was to reduce the production rate. The calculations also indicated that the approach of increasing the dryer temperature was not a fruitful route to improved performance. They showed that if the dryer temperature were increased from 200 to 225°F, at the same residence time and sweep gas rate, the hexane concentration would decrease from 75 to 65 ppm.

From these calculations, it was obvious that the only valid test of plant operating conditions was to reduce the polymer production rate from 20000 to 14000 lbs/hr. The plant test of operating at reduced rates was the preferred test compared to a plant test of the old catalyst since it would be quicker. Introducing the old catalyst into the reactors would require significant

residence time to completely displace the new catalyst from the entire system prior to the dryer. In addition, continuing to use the new catalyst was mandatory. So the plant test of returning to the old catalyst just confirms that the new catalyst is responsible for the problem. A plant test of increasing the dryer residence time by reducing the production to 14000 lbs/hr was successful at reducing the hexane content from 75 to 25 ppm. The “K” value did not change as the residence time was increased.

Step 5: Recommend Remedial Action to Eliminate the Problem without Creating Another Problem

Since the plant test of operating at reduced rates was successful and a study of changing the catalyst to produce a more porous structure indicated that other desirable catalyst attributes would be lost if the porosity was changed, it was decided to add an additional dryer. This additional dryer would provide the necessary residence time. Since the dryer addition would take several months, it was decided to return to using the old catalyst in the interim. When use of the old catalyst resumed, the mass transfer coefficient increased from 0.16 1/minutes to the previous value of 0.25 1/minutes.

8.6 LESSONS LEARNED

If daily monitoring of the “K” value were being done, it would have been possible to determine immediately that there was likely a drying problem associated with the new catalyst. As often happens in a plant test, there is only a minimal potential problem analysis conducted prior to the test. This often leads to a panicky approach to problem solving. Chapter 11 discusses approaches for conducting successful plant tests.

If drying problems had been anticipated prior to the plant test of the new catalyst, it would have been possible to use laboratory techniques to determine the magnitude of the difference in mass transfer coefficients. An apparatus such as a thermal gravimetric analyzer (TGA) could have been used to determine the mass transfer coefficient for polymer produced with both catalyst systems. While the exact absolute values of the mass transfer coefficient determined in this fashion may not have been the same as that in the plant, the relative values would have been very accurate. That is, the TGA would have likely predicted that the mass transfer coefficient (K) would have been 35 percent lower with the new catalyst.

The model of the dryer that was developed is a good example of a simple, but valuable tool for doing process analysis work. The driving force of the actual concentration less the equilibrium concentration ($X - X_e$) is theoretically correct and easy to determine. Experimental relationships such as equation (8-6) may not be available. However, there are calculation methods available to approximate the relationship between the vapor phase concentration of the

solvent and the concentration of solvent in the solid. One of these techniques is discussed in Chapter 12. The mass transfer coefficient can be determined from plant data. It is subject to error if there is a significant change in the polymer morphology. For example when the catalyst was changed, the mass transfer coefficient changed. However, it did not change when the production rate was reduced.

The calculations that were done to estimate the impact of changing plant operating conditions were performed very quickly once the spreadsheet described above was completed. The more expensive alternative of running multiple plant trials to test any *reasonable* hypothesis would have taken much more time and been much more expensive.

8.7 EXAMPLE PROBLEM 8-2

Several of the tube metal temperature indicators in an operating furnace were indicating considerably hotter than anticipated when compared to historical values. Operations personnel were not concerned since this furnace was operating at normal heat duties; normal process fluid temperatures and the furnace had never shown any tendency to foul. They concluded that the tube metal temperature indicators must have failed due to the harsh furnace environment. The technical problem solver did not believe that *all* of the tube metal indicators could have failed. A schematic diagram of this problem is shown in Figure 8-4.

The current operating data and the historical operating data are shown in Table 8-4. There were no other data available in the computer archives.

Even though this problem was discovered by the technical problem solver rather than being delivered to him by a request from operations management, it is still a valid problem that can be approached using the five-step procedure. Because of the belief of operations personnel that there was not really any problem, Step 1 had to be approached in a different fashion than in other problems described previously.

Table 8-4 Furnace data

	Historical	Current
Tube metal temperature, °F	600 to 650	750 to 900
Gas temperatures		
Entering convection section, °F	1200	1300
Leaving convection section, °F	650	700
Excess oxygen, percent	15	15
Heat absorbed, MBTU/hr	80	80
Circulation to furnace k-lbs/hr	700	700

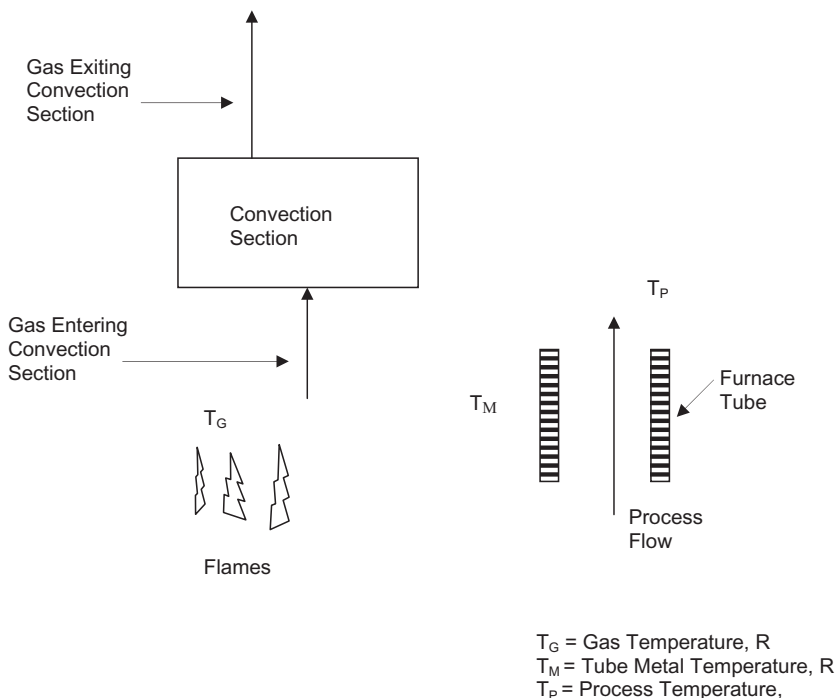


Figure 8-4 Furnace schematic.

Step 1: Verify that the Problem Actually Occurred

Step 1 required that careful examination be given to operation management's contention that there was really no problem with the indicated high tube metal temperatures. It was important that the problem solver convince himself, as well as the operations personnel, that there was a problem. If operations personnel were going to be expected to cooperate on any plant tests, they needed to be convinced that there was a problem. One of the first things that the problem solver had to do was understand how the tube metal temperature indicators were designed and installed. These thermocouples are different than normal ones in that they must measure the temperature of the furnace tube without being impacted by the radiant heat from the furnace flames. The problem solver obtained information from both instrument technicians and instrument engineers to make sure that he understood the technology of tube metal temperature indicators. Once he understood this technology, he recognized that while tube metal temperature indicators do fail, they almost always fail in such a fashion that the failure is obvious. That is, they read ridiculously high or low. Failed tube metal temperature indicators will normally have "up-scale burnout". That is, they will read ridiculously high. He also recognized that if fouling had occurred on the inside of the tube, there would be other

indications of fouling besides elevated tube metal temperatures. The problem solver decided to investigate whether there were other indications of fouling. He used the basic equation shown below to describe the radiant heat transfer that is occurring in the furnace:

$$Q = C_1 * (T_g^4 - T_m^4) = C_2 * (T_m - T_p) \quad (8-12)$$

Where:

Q = the heat transferred to the process. This is equal to the heat transferred from the gas flame by radiation. In addition, it must also be equal to the heat transferred through the tube to the process fluid.

T_g = absolute temperature of the gas in the radiant section of the furnace

T_m = absolute temperature of the tube metal

T_p = absolute temperature of the process fluid in the tubes

C_1 = a constant that is related to the type of flame. It should not change unless the type of fuel changes.

C_2 = the product of the heat transfer coefficient and the area of the tubes. It will only change if the heat transfer coefficient changes.

He noted that if the tube metal temperature (T_m) increases at constant heat duty (Q), it must be due to a decrease in the heat transfer coefficient since the area of the tubes will not change. This decrease in heat transfer coefficient could be caused by a change in fluid circulation rate or tube fouling. Since the process flow rate to the furnace is constant, the decrease in heat transfer coefficient is likely due to tube fouling. In order to achieve the same heat duty at the higher tube metal temperature, the gas temperature (T_g) must also increase. Thus, the increased gas temperature shown in Table 8-4 was confirmation that the tube metal temperature had increased. A secondary confirmation was the higher than normal gas temperature leaving the convection section, which is also shown in Table 8-4. The higher temperature gas entering the convection from the radiant section would not be cooled to as low a temperature as historical data would indicate since the heat transfer area in the convection section was fixed. Using this logic, the problem solver convinced the operations management that there *might* be a fouling problem in the furnace tubes.

Step 2: Write Out an **Accurate** Statement of What Problem You Are Trying to **Solve**

An accurate statement of the furnace problem is as follows:

“Tube metal temperatures on the process furnace are indicating that the tubes are partially fouled with deposits. Since a furnace shutdown to inspect and pos-

sibly replace the tubes will require a plant shutdown, a detailed investigation was undertaken to confirm that the tube metal temperatures are higher than normal. This investigation indicated that the tubes are very likely fouled. There is no archived data to indicate when the fouling began or if it was a gradual fouling or a one time event. While there is strong evidence that the furnace tubes are partially fouled, it is desirable to provide operations management with further evidence that the furnace is fouling and determine what steps should be taken to avoid a tube failure with a subsequent furnace fire. In addition, it will be necessary to determine why the tubes in this furnace are fouling when based on operation personnel's memory this has never happened in the past."

Step 3: *Develop* a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible

In this example problem, Step 3 is different than in previous problems. The thrust is to convince operations that a problem exists with the furnace. As discussed earlier, the logic path that was developed was partially successful in convincing operations management that there really was a fouling problem. In addition to this, consideration was given to alternative means to measure the tube metal temperatures. One possibility was to use infrared temperature measurements through a furnace peephole. Besides confirming the tube metal temperature measurements, this would also allow determining where the hottest points were. The measurements based on tube metal temperature indicators are only single points in a few tubes. A much hotter point might exist in another location. An infrared scan was conducted on the furnace tubes. The thermocouples were verified and even hotter temperatures were discovered at spots where no tube metal indicators existed.

The furnace history was considered by asking such questions as:

- When did the fouling begin?
- Did it coincide with an upset of a magnitude never before experienced?
- Has the furnace been operating for a longer continuous period than previous experience?

In addition to these questions, the questions from Chapter 5 were used to help develop a working hypothesis. (See Table 8-5)

The following was developed as a working hypothesis:

"The higher than normal tube metal temperatures in the furnace appear to be correct based on both gas temperatures and an examination of the instrument specifications which indicates that the thermocouples are "up-scale burnout" (if they fail they will read ridiculously high). In addition, an infrared scan indicates that these thermocouple measurements are correct and that there are even

Table 8-5 Questions/comments for Problem 8-2

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed.
Are all instruments correct?	The instruments had allegedly been calibrated.
Are laboratory results correct?	Not applicable.
Were there any errors made in the original design?	Not applicable.
Were there changes in operating conditions?	No.
Is fluid leakage occurring?	Not applicable.
Has there been mechanical wear that would explain the problem?	Fouling of tubes.
Is the reaction rate as anticipated?	Not applicable.
Are there adverse reactions occurring?	Fouling is caused by reaction to produce coke. This reaction might be catalyzed by material present in the process. The fouling rate seems much higher than previous experience.
Were there errors made in the construction?	Not applicable. It had been 36 months since mechanical work was done on furnace.

higher temperatures on other tubes. A review of the furnace history indicates that the current run (36 months without water washing the tubes) is nearly twice the length of previous periods of operation. Historically the furnace tubes were water washed at every 18 month furnace inspection downtime. However, they were not water washed at the last downtime because it was expedient to get the furnace back in service. It is believed that this water washing removes the fouling material before it becomes thick enough to impact the furnace operation. The fouling is believed to be initiated by process catalyst residue that is entrained during process upsets.”

Step 4: Provide a Mechanism to Test the Hypothesis

In this case because of the risk of a tube failure, the only mechanism was to shut down the furnace and water wash and inspect the tubes. The downtime was timed to coincide with a period of reduced product demand so that the lost revenue was minimized. An inspection of the tubes indicated that many of them were approaching the point of incipient failure. If the tube metal temperatures had been ignored as proposed by operating personnel, it is highly likely that a furnace fire would have occurred. This not only would have caused serious damage to the furnace, but likely would have occurred at a time when full production rate was required.

Step 5: *Recommend Remedial Action to Eliminate the Problem without Creating Another Problem*

Three remedial actions were recommended. The first was to carefully monitor the tube metal temperatures during the interim period between the discovery of the problem and the furnace shutdown. This allowed for a controlled plant shutdown to replace furnace tubes rather than an emergency shutdown during a period of high product demand. The second was to water wash the furnace tubes every 18 months. The third recommendation was to monitor the C_2 value as determined from equation (8-12) on a daily basis. This would provide information on how the fouling occurred. It could have been a one-time event that caused a sudden decrease in the value or a slow continuous decrease.

8.8 LESSONS LEARNED

This actual real-life problem illustrates the value of a careful technical analysis of all operating data as opposed to only working on problems that operations or mechanical personnel consider to be important. The initial reaction of operations personnel to ignore the high tube metal temperature indicators was carefully considered as part of Step 1. In addition, the actions of the problem solver to understand the technology of tube metal thermocouples were consistent with the concept of knowing the technology before trying to solve problems.

This problem also illustrates the fact that historical data are of great value in solving problems. However, *conclusions* (the furnace tubes never foul) based on historical data or memories that are not well supported are counter-productive. In this case, all of the current data indicated that the furnace tubes were indeed fouled. Thus, it was apparent that the conclusion based on memories and/or historical data that indicated the tubes could not be fouled was in error. It is also likely that the tubes had been fouling in the past, but because the C_2 value was not being monitored, the fouling went undetected. The fouling was likely removed every 18 months when the tubes were water washed.

If the problem solver had not been aggressive to the point of creating tension, it is likely that a furnace tube failure with a subsequent furnace fire would have occurred.

8.9 EXAMPLE PROBLEM 8-3

A plant that produced and shipped a polyolefin polymer in railroad hopper cars was contacted by a TV station with a video of one of their hopper cars on fire. These hopper cars were loaded at the manufacturing plant by discharging pellet storage bins directly into the closed hopper cars. While the hopper

cars were closed to protect the product from the elements (rain, sunshine, wind, debris . . .), there were vents in the front and back of the hopper cars. Thus, the vapor space in the hopper car was essentially air at the ambient conditions plus any hydrocarbon that evolved from the polymer.

When the public relations contact appeared on the TV station to discuss the hopper car fire, he indicated that the particular polymer was not flammable and that could not have possibly caught on fire without some external source such as sabotage or excessive heat generated by a mechanical failure or malfunctioning of the hopper car equipment.

Unfortunately, shortly after this occasion, several other hopper cars arrived at different customers with blackened vapor vents and some charred polymer indicating that there had been a fire of a limited magnitude during transportation. The material that was being shipped in the hopper cars was in the form of small pellets that had been extruded after being produced in the polymerization section. The polymerization section stripped the solvent and unreacted monomer from the polymer at a temperature of 220°F and a dryer residence time of 30 minutes. In addition, during the extrusion operation, the polymer was heated in the extruder to 550°F before being pelletized and cooled in a water bath. It seemed very unlikely that there could be sufficient residual monomer or solvent that could create a fire. In addition, operations personnel knew that when the hopper cars were loaded, that they could see a great deal of static electricity being discharged inside the hopper car. They reasoned that if there was an explosive atmosphere inside the hopper car, that it would be ignited during the loading operation. They believed that the maximum concentration of hydrocarbons in the vapor space would occur during loading. They believed that during transit, the vents would create a sweep of air through the vapor space reducing the concentration of hydrocarbons.

However, because of the multiple indications of fires in the hopper cars transporting the polymer, the operations personnel requested that a technical evaluation be made of what was causing the hopper car fires.

The problem solver used the five-step procedure to methodically develop a problem solution as described in the following paragraphs.

Step 1: Verify that the Problem Actually Occurred

There was no doubt that something unusual had happened. The problem solver decided that he needed to know what product had been loaded into these hopper cars that experienced the major fire and evidence of minor fires. When he investigated the loading records, he found that all of the unusual incidents had occurred when a specific product (experimental product X3) was being produced and loaded into the hopper cars. However, not all hopper cars loaded with this product showed evidence of flash fires. He recognized that this product was one that had to be produced at reduced rates to insure that the volatiles (unreacted monomer and solvent) were adequately stripped. He

knew that rates had recently been increased by modifications to the operating procedures and directives.

Step 2: Write Out an Accurate Statement of What Problem You Are Trying to Solve

The problem solver wrote out the following problem statement:

“There are indications that flash fires are occurring in some of the railroad hopper cars loaded with experimental product X3. The indication of these flash fires was noticed after beginning to use the recently instituted operating procedures and directives. While actual damage was minimal, there was a great deal of customer dissatisfaction. Determine the cause of the flash fires. This analysis should include the observation that not all hopper cars loaded with this product showed signs of a fire. Once the cause has been determined, provide recommendations for eliminating the flash fires. In addition, any recommendations should provide for shipping a product that meets the Department of Transportation (DOT) regulations.”

Step 3: Develop a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible

In addition to the observations described above, the questions from Chapter 5 were used to help develop a working hypothesis. These questions are shown in Table 8-6.

After reviewing the data and the questions above, three possible hypotheses were developed as follows:

1. The new operating directives and procedures were causing excess quantities of unreacted monomer or solvent to be left in the polymer, which then accumulated in the hopper car and formed an explosive mixture. This mixture could then be ignited by an undefined ignition source.
2. There were changes in the catalyst which now resulted in a less porous polymer particle. Thus, the temperature and residence time that were previously used successfully in a plant test to demonstrate the new procedures for X3 were no longer adequate. Again if this happened, it was theorized that the excessive quantities of solvent and unreacted monomer accumulated in the hopper car and formed an explosive mixture.
3. There was a change in the adequacy of stabilization so that the polymer decomposed in the extruder. This decomposition resulted in the formation of volatile materials which then did not vent out of the extruder because of the short residence time. They were trapped in the pellet and were carried into the hopper car where they evolved from the pellet and accumulated and formed an explosive mixture.

Table 8-6 Questions/comments for Problem 8-3

Question	Comment
Are all operating directives and procedures correct and being followed?	All were being followed. However, there had been recent changes to the directives and procedures. Some of these appeared highly questionable.
Are all instruments correct?	The instruments used to monitor the stripping operation were calibrated weekly.
Are laboratory results correct?	The volatiles results were not routinely measured. It was believed that maintaining adequate temperature was all that was required to maintain volatiles control.
Were there any errors made in the original design?	Not applicable.
Were there changes in operating conditions?	Yes. See above.
Is fluid leakage occurring?	Not applicable.
Has there been mechanical wear that would explain the problem?	Not applicable.
Is the reaction rate as anticipated?	Not applicable.
Are there adverse reactions occurring?	Unknown changes in the catalyst might create a polymer with a less porous structure that would make volatiles removal more difficult. This could be detected by bulk density measurements. In addition, the polymer might be decomposing in the extruder forming volatile materials.
Were there errors made in the construction?	Not applicable.

It was clear after considering these three hypotheses that all of them had a common thread. The common thread was twofold. In the first place, the hydrocarbons (solvent and unreacted monomer) had to build up to the point of forming an explosive mixture. The second aspect of this hypothesis was that the explosive mixture was ignited by an ignition source. This ignition source could have been something dramatic like a lightning strike or something as commonplace as static electricity. The movement of pellets in the hopper car while it was in transit could well generate sufficient static electricity to create an ignition source. This would be particularly true if the relative humidity of the air in the vapor space was very low. The problem solver used the traditional process engineering safety assumption—that is, when dealing with an explosive mixture, an ignition source will always be found if the mixture is in the explosive range for a sufficient amount of time. Thus, he only considered which hypothesis should be investigated for how an explosive mixture formed.

Table 8-7 Data for evaluation

Item	Value
Hopper car capacity, lbs of polymer	180000
Hopper car fill volume, percent	70
Bulk density of the polymer, lbs/ft ³	25
Skeletal ⁽¹⁾ density of the polymer, lbs/ft ³	56
Vapor pressure of monomer at 100 °F, psia	220
Molecular weight of monomer	42
Explosive range of monomer ⁽²⁾ , volume percent	
Lower	2
Upper	11

(1) Skeletal density is the density of the polymer if the particle had no voids.

(2) Since essentially the entire hydrocarbon was unreacted monomer, no consideration was given to the solvent. In addition, it should be noted that for gases the volume percent and mol percent are identical.

All of the three hypotheses required that the gases accumulate in the vapor space to form an explosive mixture. The first question that the problem solver had to answer was “How much hydrocarbon had to be left in the polymer for an explosive mixture to form in the vapor space of the hopper car?”

It was necessary to develop some basic data before the problem solver could begin to assess this question. The data that he developed to help assess this problem are shown in Table 8-7.

In order to test the hydrocarbon accumulation hypothesis, the following calculations were done to determine how much hydrocarbon would be left in the polymer entering the hopper car for an explosive mixture to accumulate in the hopper car vapor space. These calculations assumed that the polymer had been in the hopper car for such an extended period of time that equilibrium between the vapor space and the polymer was reached. The calculations also ignore the purging of the vapor space that might occur as the hopper car traveled to the customer. As such, they represent the worst-case scenario. However, the case might occur if the hopper car sat stationary on the railroad track for an extended period of time with a minimal amount of wind. It was assumed that the equilibrium relationship given in equation (8-6) shown below was applicable for this polymer.

$$X_E = 295000 * (P/VP)^{1.5} \quad (8-6)$$

$$F = V + S \quad (8-13)$$

Where:

F = total monomer in the hopper car, lbs

V = monomer in vapor space, lbs

S = monomer remaining in polymer at 100°F, lbs

$$\begin{aligned} T &= Ca * 100 / (BD * FV) \\ &= 180000 * 100 / (25 * 70) = 10285 \text{ ft}^3 \end{aligned} \quad (8-14)$$

$$\begin{aligned} VT &= T - Ca / SD \\ &= 10285 - 180000 / 56 = 7070 \text{ ft}^3 \end{aligned} \quad (8-15)$$

Where:

T = total volume of hopper car, ft³
 Ca = polymer capacity of hopper car, lbs
 BD = bulk density of polymer, lbs/ft³
 FV = volume of hopper car filled with polymer, percent
 VT = vapor volume of hopper car, ft³
 SD = skeletal density of polymer, lbs/ft³

Note that VT includes the volume associated with the pores in the polymer.

$$\begin{aligned} P &= LEL * \Pi / 100 \\ &= 2 * 14.7 / 100 = 0.294 \text{ psia} \end{aligned} \quad (8-16)$$

Where:

LEL = the lower explosive limit, volume or mol percent
 Π = the total pressure, psia

$$\begin{aligned} D &= MWM * 520 / (379 * (460 + 100)) \\ &= 42 * 520 / (379 * 560) = 0.1029 \text{ lbs/ft}^3 \end{aligned} \quad (8-17)$$

Where:

D = density of monomer gas, lbs/ft³
 MWM = molecular weight of the monomer

$$\begin{aligned} V &= LEL * D * VT / 100 \\ &= 2 * 0.1029 * 7070 / 100 = 14.55 \text{ lbs} \\ X_E &= 295000 * (P / VP)^{1.5} \\ &= 295000 * (0.294 / 220)^{1.5} = 14.4 \text{ ppm} \end{aligned} \quad (8-6)$$

$$\begin{aligned} F &= V + S \\ &= 14.55 + 14.4 * 180000 / 1000000 = 17.14 \text{ lbs} \\ &= 95 \text{ ppm of monomer in the incoming polymer} \end{aligned} \quad (8-13)$$

Thus, if the polymer going to the hopper contained more than 95 ppm of monomer, the vapor space could well be at the LEL.

The problem solver investigated the current operating directives and procedures and their bases. When he did this investigation, he found that the approach to setting the new directives and procedures had been strictly empirical with no consideration to the theory and time elements of diffusion. A test run had been conducted by establishing the new conditions and rates in the polymerization and extrusion sections. When the conditions were well established, samples downstream of the extrusion and pelletizing operations were collected in an open-mouth container. A conventional gas explosivity analyzer was inserted into the container immediately after the sample was collected and the percent LEL was measured. The explosivity analyzer gives a reading of the percent of the LEL (lower explosive limit). For example, if the vapor space were at the LEL, the analyzer would read 100 percent. Thus, percent LEL is a measure of the approach to the lower explosion limit.

In this test of X3, it was believed that measuring the vapor space immediately would give the highest value since the monomer in the vapor phase of the open container would not have time to diffuse into the surrounding air. A single measurement was made and since the percent LEL was less than 100 percent, it was concluded that the new conditions and rates would produce a product that would satisfy the DOT regulations. These regulations stated that the vapor space of products shipped in hopper cars should be below the LEL. Obviously if the vapor space in the hopper car was below the LEL, it would not ignite.

In addition, the problem solver reviewed the bulk density measurements. The experimental polymer (X3) actually had a slightly lower bulk density than the normal polyolefin products. Thus, it appeared that the product would be more porous than the conventional product. He also reviewed the current stabilizer and found that it was the same that had been in use for several years. This cursory review did not mean that he had ruled out hypotheses 2 and 3 conclusively. But it did indicate that these were unlikely to be the simplest root cause. Following the concept of taking the simplest route whether it is the root cause or a calculation technique, the problem solver developed the following theoretically correct working hypothesis.

“It is believed that the hopper car fires and product charring that occurred when shipping X3 are associated with the residual monomer that remained with the polymer when the new rates and operating conditions were used. While the vapor space above the pellets was not in the explosive range immediately after they were loaded into the hopper car, the evolution of vapors from the polymer over time allowed an explosive concentration to build up in the hopper car vapor space. While it is uncertain what the source of ignition was, it is known that static electricity is almost always present due to the movement of the polymer particles. Whether this explosive mixture ignited and to what degree a fire occurred depended on three factors:

1. The movement of the hopper car. If the hopper car was continuously in motion, there was a high probability that some of the vapors would be replaced by air and the vapor phase concentration might be reduced to a level below the lower explosive limit.
2. The humidity of the ambient air. If the humidity was high in the hopper car, it is unlikely that a static discharge would occur.
3. The temperature. If the temperature of the polymer in the hopper car was elevated (due to the ambient temperature), then there is a higher probability of a major fire occurring rather than a flash fire that chars some of the polymer on the top of the hopper car.

In order to eliminate this problem, the production rates of X3 should be reduced to the previous levels. In addition, the new operating directives and procedures should be abandoned.”

Step 4: Provide a Mechanism to Test the Hypothesis

Two mechanisms were provided to test the hypothesis. On the next X3 run, the rates were reduced to the previous levels. The percent LEL was measured in the vapor space of each hopper car after 24 hours and prior to shipping. In each case, the percent LEL was well below 100 percent. There were no reports of charred polymer or fires even though the customers had been alerted to watch for such events. In addition during the run, samples were taken of the product leaving the pelletizing section in the same fashion as discussed earlier. The percent LEL was determined as a function of time and Figure 8-5 was used to illustrate the buildup of the percent LEL as a function of time. Thus, it was concluded that reducing the production rates was a successful test of the hypothesis.

Step 5: *Recommend Remedial Action to Eliminate the Problem without Creating Another Problem*

The recommendation to operate at reduced rates could only be considered an interim recommendation. The problem solver used some of the techniques described in Example Problem 8-1 and concluded that the only way to operate at full rates while producing this polymer was to add additional dryer residence time. He recommended that a study be initiated to determine whether the economics of producing X3 could justify either operating at reduced rates or adding a larger dryer.

8.10 LESSONS LEARNED

There were pressures to increase the production rates of X3. It was obvious in hindsight that these pressures caused a blatantly flawed empirical test to be developed. The conclusion that rates could be increased was based completely

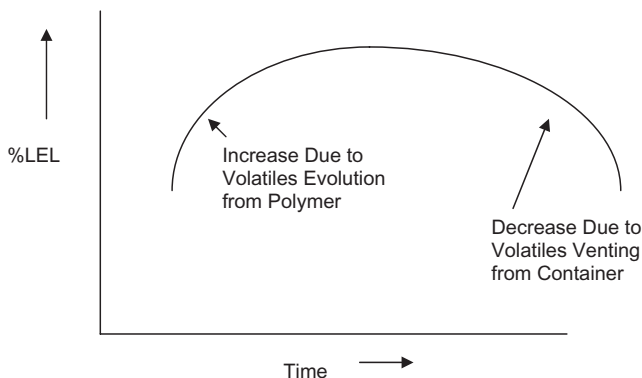


Figure 8-5 Percent LEL versus time.

on this flawed test with no theoretical calculations. This empirical test overlooked the obvious—that vapor evolution from the polymer that occurred over time might cause a maximum in the relationship between percent LEL and time. This maximum could well be above the LEL. The risk of this approach could have been discovered if theoretical calculations had been done to determine what the maximum equilibrium concentration of monomer in the vapor phase of the sample container would be. This calculation would require that the concentration of the monomer in the polymer leaving the pelletizing section be known. The concentration of monomer in the vapor phase could then be calculated using the techniques described earlier and with the assumption that none of the monomer dispersed into the atmosphere from the container.

There are times when theoretical calculations are more accurate than obtaining laboratory results. In this case, if the concentration of monomer in the polymer could be analyzed and the equilibrium relationship was available (equation (8-6) for example), then the *maximum* equilibrium vapor phase concentration and hence the percent LEL could be determined easily. This would be more accurate than the maximum percent LEL determined by the explosivity meter. This is because the explosivity meter only measures the percent LEL at a point in time which is likely not to be the maximum concentration.

The failure to do a detailed theoretical analysis of the proposal to increase rates by modified operating directives and procedures was costly. It gave the company adverse publicity and adverse relationships with their customers. Their customers had never seen charred polyolefin products from the company or any other company that they purchased material from. The approach also cost problem-solving time. Instead of starting to understand the monomer removal limitation when X3 was first discovered to have a limitation, the empirical approach caused the start of problem-solving activities to be delayed.

In addition, problem-solving activities were diverted to understanding the hopper car fires as opposed to eliminating the drying limitation.

The approach of asking customers to be on the watch for charred polymer might seem to be “just asking for trouble”. However, it was mandatory to confirm that the plant test of operating at reduced rates was truly successful. The failure to get this information would have likely resulted in a failed test since enough data would not be present to prove or disprove the hypothesis.

Chapter 8 Table of nomenclature

BD	The bulk density of polymer, lbs/ft ³
C	A constant referred to as the “lumped parameter constant”. If it is related to heat transfer, the constant is generally taken as $U \cdot A$. If reaction is involved, it is simply set equal to “ C_R ” in this chapter. If drying or stripping is involved, the value “ K ” is used in this chapter
C_R	The lumped parameter constant for reaction (reaction rate constant)
C_E	A constant that relates equilibrium of solvent in polymer to the vapor phase composition. It can be determined from experimental data or approximated by application of theoretical relationships
C_1	A constant that is related to the type of furnace flame. It should not change unless the type of fuel changes
C_2	The product of the heat transfer coefficient and the area of the tubes. It will only change if the heat transfer coefficient changes
Ca	The polymer capacity of the hopper car, lbs
DF	The driving force or incentive for mass or heat transfer to occur
DF_R	The driving force for radiant heat transfer
dX/dt	The rate of disappearance of component X by reaction or stripping
F	The total monomer in the hopper car, lbs
FV	The volume of the hopper car filled with polymer, percent
K	The lumped parameter constant for drying or stripping. It is somewhat related to diffusion. Since it deals with mass transfer, it is also referenced in this chapter as a mass transfer coefficient
LEL	The lower explosive limit, volume or mol percent
$\ln \Delta T$	The log mean temperature difference or the driving force for heat transfer
P	The partial pressure of the solvent in the vapor phase

Q	The rate of heat transfer
R	The rate of change with time of the variable under study. It could be heat transfer, reaction rate or volatile stripping
S	The monomer remaining in polymer at 100°F, lbs
SD	The skeletal density of polymer, lbs/ft ³
T	The total volume of the hopper car, ft ³
t	The amount of time in the dryer, minutes
T _p	The absolute temperature of the process fluid in the tubes
T _g	The absolute temperature of the gas
T _m	The absolute temperature of the tube metal
U*A	The lumped parameter (C) or for heat transfer the heat transfer coefficient multiplied by the area
V	The monomer in vapor space of the hopper car, lbs
VP	The vapor pressure of the solvent at the dryer temperature
VT	The vapor volume of the hopper car, ft ³
(X - X _e)	The driving force for stripping
X	The actual concentration of solvent in a polymer
X _e	The equilibrium concentration of solvent in the polymer
X	The concentration of component X
Y	The concentration of component Y
X _f	The concentration of solvent in the outlet polymer
X _o	The concentration of solvent in the inlet polymer
Π	The total pressure, psia

APPLICATION TO UNSTEADY STATE

9.1 INTRODUCTION

While most process engineering courses deal with design and operations at steady-state conditions, industrial processes operate at constantly changing conditions. Frequently the differences between steady and dynamic conditions can be ignored. However, an approach to considering unsteady operations will be of value to every process engineer. There are multiple instances of unsteady-state operations that a process engineer must often consider. Start-ups are never steady state and this is probably the most challenging phase of problem solving. This is often an area where the intuition of an experienced operator or engineer is more valuable than a detailed problem-solving activity. However, there are examples where a frequently encountered start-up activity that involves a problem (reactor start-up for example) can be approached using some of the principles outlined in this book.

Batch operations are always dynamic. If problems are uncovered during a batch operation, typical process engineering calculations based on steady-state operations will rarely be of any value. Thus, the industrial problem solver needs to have tools to allow him to approach these dynamic operations. Example Problem 9-1 is a typical batch operation real-life example.

Unsteady-state upsets can often provide valuable information. For example, short-term upsets caused by feed impurities can be extrapolated to steady-state values using techniques that relate the time of the upset to the actual reactor residence time. This will allow the problem solver to determine the steady-state impact of these impurities. This is the impact on the process that

would occur if the short-term impurity concentration in the feed were at the upset level consistently. This information can be used to determine the specification of the impurity in the feed.

9.2 APPROACH TO UNSTEADY-STATE PROBLEM SOLVING

The most difficult aspect of solving unsteady-state problems in an industrial environment is the balance between formulating technically correct hypotheses and the need for expediency. This was referred to in Chapter 3 as *optimum technical depth*. Because of the difficulty of determining this balance, one of two extremes is often present. In one of these extremes, the problem solver begins developing a highly sophisticated dynamic model that requires a powerful computer to solve the differential equations. As the work slowly progresses, management becomes impatient and cancels the project. At the other extreme, the problem solver often “gives up” and uses intuitive “gut feel” rather than developing a simplified dynamic model. *Optimum technical depth* is the approach used to achieve a balance between these two extremes. This balance will be a strong function of the environment surrounding the problem. For example during a start-up, a balance slanted toward intuition is likely the best approach. On the other hand, a chronic problem which does not have any apparent answer will require a more sophisticated approach. The following paragraphs present guidelines for approaching unsteady-state problems.

If the problem requires an *immediate* recommendation such as during a start-up, the best approach will be to rely on the instinct of an operator or experienced start-up engineer. Medical research has shown that our minds work by both instinct and logical reasoning. Obviously instinct is faster than development of a detailed logical path. Minds conditioned by years of experience with unsteady-state operations such as a start-up will react instinctively to provide immediate response as opposed to having to think about the situation.

The basic concept for considering unsteady-state operations is equation (9-1) shown below:

$$AD = I - O - RD \quad (9-1)$$

Where:

AD = rate of accumulation. This could be accumulation of anything—level, heat or reactant

I = inflow of material or heat

O = outflow of material or heat

RD = removal/addition of heat, or formation/destruction of material by reaction

This relationship can be used as a building block for all unsteady-state considerations from something as simple as the change of level in an accumulator to the development of complicated dynamic models. The thrust of this chapter is the development of simple, but accurate dynamic models.

If it is considered desirable to build a dynamic model of the unsteady-state process, all physical components of the system must be considered. For example, with steady state, the heat capacity of the process vessel is correctly never considered. However, for unsteady-state heat balances, the heat capacity of the vessel (walls and contents) must be considered and will often be a moderating influence. This moderating influence will cause the rate of temperature change to be less than calculated if the heat capacity of the vessel is ignored. The dynamic model should be kept simple by use of the perfectly mixed vessel or plug flow assumptions where appropriate, use of lumped parameter constants (such as overall heat transfer coefficients) and an assumption of uniform metal temperature.

If reaction is involved, it should be recognized that there are two models that can be used to simulate an unsteady-state reaction. Traditional process engineering indicates that the reaction rate is proportional to the concentration of the reactant. That is, the rate of reaction will be increasing as the concentration of the reactant in the vessel increases. This has been referred to as the “slow response model”. For some reactants such as impurities in a polymerization reactor, the impurity reacts as soon as it enters the reactor. This “fast response model” is easier to develop because it allows assuming that the concentration of the impurity in the reactor approximates zero. In order to determine whether the traditional model or the “fast response model” should be used requires that the problem solver understand the technology. As a general rule, the “fast response model” will apply only to reaction impurities in a polymerization reaction. Most other reaction modeling will be more accurate if the traditional process engineering approach is utilized. Regardless which model is used, short-term upsets and fundamental models of stirred tank or plug flow reactors can be used to estimate the full impact of an impurity.

9.3 EXAMPLE PROBLEMS

The problem-solving techniques associated with unsteady-state operations are illustrated by the actual case histories described in the following paragraphs. Problem 9-1 illustrates the use of these techniques for solving a problem associated with a batch reactor that experienced a temperature “runaway” (such a rapid temperature increase that the emergency devices were activated). Problem 9-2 illustrates the use of these techniques to extrapolate short-term reaction upsets caused by an impurity to steady-state conditions.

9.4 PROBLEM 9-1

A batch reaction was carried out in a reaction vessel with a cooling water jacket. The reaction was initiated when the primary reactant was added to the reaction vessel. The primary reactant was dissolved in hot hexane in a small vessel and then pressured into the reaction vessel with nitrogen as fast as possible. While the technology had been developed in the research facility of a major petrochemical company, the actual manufacturing of the material was being done by a contract manufacturer. His operation was designed and operated on an exceptionally low budget. There were no flow instruments to measure and control the rate of addition of the reactant. The average rate of reactant addition was obtained knowing the amount of material in the small vessel and the time that it took to add it to the reaction vessel.

The exothermic reaction had been conducted successfully many times. However, during a recent batch, a rapid increase in temperature was experienced as the primary reactant was added to the reactor. The rapid temperature increase was so fast and of such a magnitude that the safety release system on the reactor was activated. The actual manufacturing location was located several hundred miles away from the technology center. Operations personnel decided to solve the temperature runaway problem without asking for help from the technology center. In order to eliminate the rapid increase in temperature, operations personnel decided to add the reactant at a very slow rate. The next batch was produced without a temperature runaway. However, the product produced in this fashion did not meet the product morphology specifications. After this batch failed to meet the morphology specifications, the operations personnel requested help from the technology center. The problem solver was charged with the responsibility of determining how to conduct this reaction with an 80 to 90 percent probability that a second temperature runaway would not occur and that the product morphology would be satisfactory.

The problem solver began accumulating technology information. It was known that the primary reactant reacted instantly when it entered the reactor (fast response model). It was desirable to add the reactant as fast as possible for two reasons. As indicated earlier, the morphology of the product was adversely impacted by a slow addition rate of the reactant. In addition, the heat of reaction provided heat input to raise the reactor temperature rapidly from 149 to 185°F.

The heat of reaction was unknown. It was not determined in the laboratory during the development part of the project. Actually, the laboratory chemists believed that there was no heat of reaction. The small-scale reactor had an inherently high area-to-volume ratio. In addition, this laboratory scale reactor was surrounded by a constant temperature sand bath. This combination essentially eliminated the chance to observe any heat of reaction in the laboratory. The nature of the reaction was such that the heat of reaction could not be

determined by classical literature approaches. In addition, time and financial constraints did not allow determining this variable from laboratory data.

The problem solver began using the five-step problem-solving approach described earlier as is shown below.

Step 1: Verify that the Problem Actually Occurred

Verification of this problem was easy since the hexane vapor from the safety release system on the reactor (a rupture disk) condensed in the air and “rained” on a local veteran’s day parade. There were no injuries, but several uniforms and band instruments required cleaning and reconditioning. In addition, a review of the reactor temperature and pressure data indicated that the rupture disk did not release prematurely. That is, the pressure and temperature had really gotten out of control.

Step 2: Write Out an *Accurate* Statement of What Problem You Are Trying to *Solve*

The problem statement developed by the problem solver was as follows:

“An exothermic reaction conducted in a batch reactor had a temperature runaway even though the same reaction had been conducted many times previously with no temperature runaway. In a subsequent batch it was demonstrated that the temperature could be controlled by using a slow rate of addition of the primary reactant. However, it is necessary to add the primary reactant at a rapid rate in order to obtain the desired product morphology. Determine what caused the batch reactor to have a temperature runaway. In addition, develop procedures that insure that there is at least an 80 to 90 percent confidence level that this temperature runaway will not reoccur when producing a product that meets the morphology specifications.”

Step 3: *Develop* a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible

Table 9-1 shows the questions from Chapter 5 along with appropriate comments.

A review of the comments associated with these questions and a review of all previous runs indicated several points of interest that would require additional considerations. These were as follows:

- While the batch size was the same, the rate of reactant addition varied greatly from run to run. As indicated earlier, this rate of addition was only determined after completion of the addition since there were no flowmeters on the transfer line. There were no procedures given for the rate of reactant addition. Some operations personnel pressured the drum used to mix the reactant and hexane with nitrogen prior to opening the transfer

Table 9-1 Questions/comments for Problem 9-1

Question	Comment
Are all operating directives and procedures being followed?	For the batch that had a temperature runaway, all appeared to have been followed. However, there were no guidelines given for how fast to add the primary reactant.
Are all instruments correct?	The instruments had allegedly been calibrated.
Are laboratory results correct?	The product morphology on the second batch was confirmed by two independent techniques.
Were there any errors made in the original design?	Yes. The laboratory chemists indicated that there was essentially no heat of reaction based on their studies. In hindsight, this was obviously in error.
Were there changes in operating conditions?	Yes. Rate of addition of reactant was highly variable even though batch sizes were the same.
Is fluid leakage occurring?	Not applicable.
Has there been mechanical wear that would explain the problem?	This is possible, but it would cause the heat removal capability to decrease. This was not occurring based on measured coolant flows and temperatures.
Is the reaction rate as anticipated?	Reaction rate was highly dependent on reactant rate of addition.
Are there adverse reactions occurring?	Adverse reactions were likely the cause of poor morphology. However, this is exceptionally complicated chemistry. Thus, solving the morphology problem while maintaining slow addition of reagents is unlikely.
Were there errors made in the construction?	Not applicable. Some batches worked fine.

valve. Others simply started the nitrogen flow to pressurize the drum and then opened the transfer valve. There were times when the mixing drum was hotter than in other times, which impacted the solution viscosity, which would affect the rate of reactant transfer.

- While the laboratory chemists reported that the heat of reaction was insignificant, there had to be a significant heat of reaction to cause the vessel contents to increase from 149 to 185°F in a short period of time. If the heat of reaction was known or could be determined, it would be possible to estimate the rate of temperature increase for any batch size and/or rate of reactant flow.
- In addition to the problem batch, there were several other runs where the temperature increased *almost* as rapidly; however, the reactor temperature did not become unstable. The only difference in these runs was the rate of reactant addition.

While it could be theorized at this point that the temperature runaway was due to the rate of reactant addition, this theory would only allow one to specify that an addition rate equivalent to that of the first failed batch would cause a temperature runaway. It would not allow determination of the maximum rate of reactant addition. A more fundamental approach was required to allow specifying the target reactant addition rate.

The problem solver decided to approach the problem using a fundamental approach. He felt that if he could express the factors involved in the temperature runaway mathematically, he could understand better how to prevent it. A temperature runaway occurs when the rate of heat generated is greater than the maximum rate that heat can be removed. This can be expressed mathematically as follows in equations (9-2) through (9-4):

$$Q_g > (Q_r)_{\max} \quad (9-2)$$

Where:

Q_g = the rate of heat generation, BTU/hr

$(Q_r)_{\max}$ = the maximum rate of heat removal, BTU/hr

$$Q_g = \Delta H_R * R \quad (9-3)$$

$$(Q_r)_{\max} = U * A * (T_R - T_C) \quad (9-4)$$

Where:

ΔH_R = the heat of reaction, BTU/lbs

R = rate of reaction. For the case of an instantaneous reaction, it is the rate of reactant addition, lbs/hr

U = the heat transfer coefficient, BTU/hr-°F-ft²

A = the heat transfer area, ft²

T_R = the temperature of the reactor, °F

T_C = the *minimum* temperature of the coolant, °F

Note that equation (9-4) has been simplified from the traditional heat transfer equation that involves use of a logarithmic relationship. This is valid for this particular case since the coolant is flowing through the reactor with minimal increase in temperature. The temperature to be used is the minimum coolant temperature that can be obtained. It is assumed that the control system will react to provide the minimum coolant temperature possible. In addition, because the reactor vessel is well mixed, the reactor temperature throughout the vessel is constant at any point in time.

For a batch reactor, equations (9-3) and (9-4) can be combined and a heat accumulation term can be added to take into account the unsteady-state

nature. In addition, any heat accumulation will cause an increase in the temperature of the reactor. The equations below represent this situation.

$$AC = \Delta H_R * R - U * A * (T_R - T_C) \quad (9-5)$$

$$AC = W * C_P * dT/dt \quad (9-6)$$

Where:

AC = the heat accumulation, BTU/hr

W = the weight of material (metal, water, reactants), lbs

C_P = the average specific heat of material, BTU/lb-°F

dT/dt = the rate of temperature rise, °F/hr

Since the reaction of the reactant being pressured into the reactor is instantaneous, the heat generated ($\Delta H_R * R$) depends only on the rate of reactant addition. Thus, equations (9-5) and (9-6) could be combined and modified to allow solving for the heat of reaction.

$$\Delta H_R = (W * C_P * dT/dt + U * A * (T_R - T_C)) / R \quad (9-7)$$

In the above equation, “U” and “A” can be estimated from physical dimensions and typical vessel heat transfer coefficients. Since all previous batches and future plans called for using the same vessel, obtaining exact values of “U” and “A” was not important. The product of U*A was considered a “lumped parameter constant”.

Equation (9-7) was used to determine the heat of reaction for all previous runs. Since a reasonably constant heat of reaction was calculated over a wide range of reactant addition rates (R), this approach seemed valid. After determining the heat of reaction using data from the batch runs, calculations were done to determine the maximum rate of reactant addition. Referring back to equation (9-2), a typical approach is to provide a 10 percent safety factor so that the maximum rate of heat removal is 10 percent greater than the maximum rate of heat generated. Thus, equation (9-2) can be modified as follows:

$$1.1 * Q_g < Q_{rmax} \quad (9-8)$$

In order to estimate the maximum rate of reactant addition, equation (9-8) along with equation (9-9) shown below which is rearrangement of equation (9-7), was used.

$$dT/dt = (R * \Delta H_R - U * A * (T_R - T_C)) / (W * C_P) \quad (9-9)$$

Equation (9-9) was used to estimate the maximum rate of reactant addition (R) that would allow the temperature rise from 149 to 185°F without causing

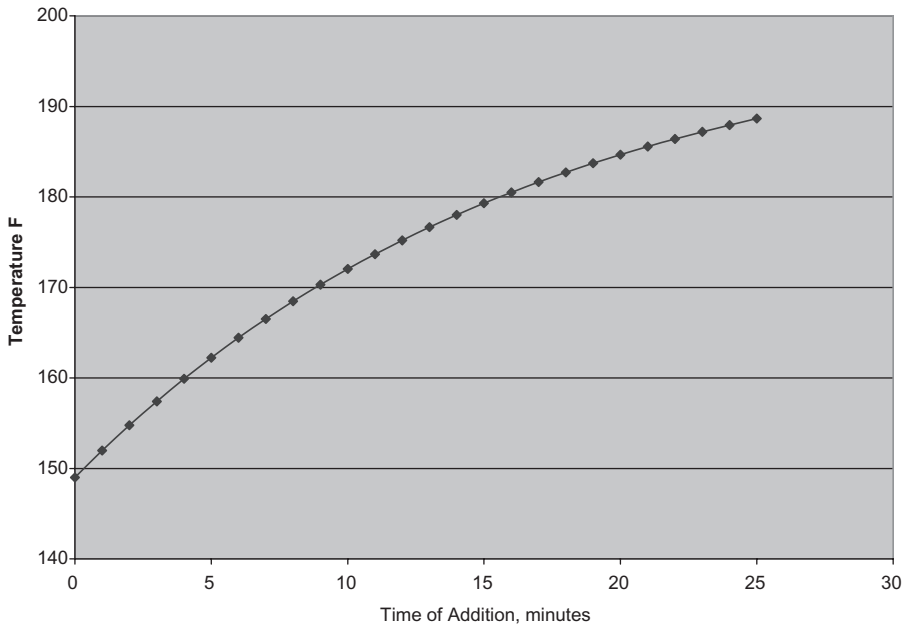


Figure 9-1 Reactor temperature versus time.

a temperature runaway. This maximum rate of addition was determined using an iterative procedure along with a spreadsheet. The calculated relationship between the reaction temperature and time for the maximum rate of addition is shown in Figure 9-1. After the maximum rate was determined, it was reduced by 10 percent to be consistent with the requirements shown in equation (9-8).

Using this approach, it was estimated that the maximum rate of reactant addition was 25 percent less than utilized in the batch on which a temperature runaway occurred. The problem solver developed the following working hypothesis:

“It is theorized that the temperature runaway was caused by rapid addition of the primary reactant. This addition rate was so high that the temperature could not be controlled even when the coolant was at the maximum rate. Calculations indicate that if the primary reactant rate addition was reduced by 25 percent the reaction could be controlled.”

Step 4: Provide a Mechanism to Test the Hypothesis

Developing a mechanism to test the hypothesis was easy from an engineering standpoint. As described above, the maximum rate of reactant addition to achieve a peak temperature of 185°F was easily estimated. However, convincing the operations personnel to add the reactant at this rate was difficult since

they recently had good success controlling the temperature while adding the reactant at a much lower rate and allowing the reactor to slowly heat up. As indicated earlier, this resulted in a product with poor morphology. In order to convince them to test the hypothesis, it was necessary to give them a complete explanation for the importance of the morphology of the product and to stand by the reactor when the reactant was added at a rapid rate. The problem solver had estimated the nitrogen pressure that would be required to transfer the reactant to the drum at the desired rate. He also had calculated the rate of level change in the reactant storage drum that would result if the reactant were added at the correct rate. The test was successful in producing a product with good morphology and the temperature rose as predicted without a temperature runaway.

Step 5: *Recommend Remedial Action to Eliminate the Problem without Creating Another Problem*

The hypothesis test (Step 4) proved that the reactant could be added at a high rate. In order to prevent another temperature runaway, additional controls were considered to assure that the target reactant addition was maintained. Since as indicated earlier the only means used by operations personnel for knowing the addition rate was the amount of time that it took to add the reactant, a more positive technique was mandatory. The project did not have funds for the installation of a flowmeter nor was the required shutdown time immediately available. Three approaches were used to insure that the reactant was being added at the correct rate. The pressure to be reached and maintained on the reactant storage drum was specified in the operating procedures. In addition, the rate of level change that would be anticipated was specified. As a final check, the curve shown in Figure 9-1 was provided and was to be used to monitor the rate of temperature rise in the first few minutes. For example, if the initial temperature increase were too fast, it would indicate that in spite of the other techniques, the rate of addition was too fast. The rate of addition would then be reduced.

9.5 LESSONS LEARNED

Although it has nothing directly to do with problem solving, one of the lessons learned was that it is very difficult to determine heat of reaction from laboratory experiments that are not specifically designed to obtain this variable. A typical laboratory experiment will be designed to obtain reaction rate variables or product quality attributes. The best way to do this will be at a constant temperature. This is usually done by utilizing small equipment that has a high area-to-volume ratio and is surrounded by a constant temperature bath. With this facility, it will be impossible to determine the heat of reaction or even to notice whether there is a heat of reaction or not.

The utilization of the unsteady-state relationship, equation (9-1), for heat accumulation proved to be a reliable tool for determining the heat of reaction. As indicated, the key to being able to successfully use this equation is the full inclusion of all of the heat content (vessel and reactants) of the process under consideration. The qualification that time and money were not available to determine the heat of reaction in the laboratory is often the case in industrial problem solving. In order to obtain the heat of reaction in the laboratory, it would have taken time and funds to build a laboratory reactor specifically designed to obtain heat of reaction data.

In problem solving, the engineering calculations are often the easiest part of the job. Convincing either operations management or the hourly workforce of operators and mechanicals that the recommended solution is correct, is often more difficult. The process of convincing the operations organization to adopt the answer will be easier if they are convinced that the problem solver is there with them to assist them if something was wrong with the calculations. Thus in this example problem, the problem solver was present when the operator added the reactant at the calculated rate. While things went as planned, the operator felt much more comfortable in setting the pressure to give the high rate of flow since the problem solver was present with him.

9.6 EXAMPLE PROBLEM 9-2

A CSTR (Continuous Stirred Tank Reactor) in a polymerization plant was plagued by short-term “loss of reaction” events. While these events were small in magnitude, they created product quality upsets, as well as a loss of catalyst efficiency. These upsets appeared to be associated with spikes of carbon dioxide (CO_2) in the monomer feed. The reactor residence time was approximately 3 hours. The short-term spikes of CO_2 lasted for only 30 to 60 minutes. Some batch data were available from the laboratory indicating that the CO_2 specification of the monomer feed currently at 10 ppm needed to be reduced. However, management would like to be convinced that the laboratory data were consistent with the plant experience. Management also believed that there was probably another impurity that was not being analyzed that was causing the problem. This belief was based on previous experience in another plant that utilized a similar, but not identical catalyst system. Management was also concerned that a project to reduce the CO_2 specification and to eliminate spikes would take several months to implement, as well as requiring significant investment. Thus, they did not want to proceed with the project unless there was a high probability of success.

The problem solver was asked to determine if these upsets were really caused by feed impurities, what the likely feed impurity was and what the impurity's real impact on the process was. It was believed that this approach would lead to determining and setting realistic impurity specifications on the feed monomer.

The problem solver approached the problem using the five-step problem-solving technique as shown in the following paragraphs.

Step 1: Verify that the Problem Actually Occurred

Verification of this problem was done by two different techniques. The polymer was analyzed to determine the concentration of catalyst in the polymer leaving the reactor. From this result, the catalyst efficiency was calculated and it was clear that during CO₂ spikes, the catalyst efficiency did decrease. However, this approach only gave an average catalyst efficiency at any point in time. In addition to this analytical approach, the calculated production rate (as determined by the process control computer using a heat balance) was used to determine the instantaneous production rate.

Step 2: Write Out an Accurate Statement of What Problem You Are Trying to Solve

The statement written by the problem solver was as follows:

“Frequent losses of reaction episodes are occurring in a polymer plant. These episodes cause a decrease in average catalyst efficiency and inconsistent product quality. These episodes appear to occur at the same time as short-term spikes of CO₂ concentration in the monomer feed. Determine the cause of the frequent “loss of reaction” episodes. Any conclusions based on plant data must be consistent with available laboratory data on the impact of CO₂ on the polymerization reaction. This evaluation should also indicate whether or not there is any indication that another impurity besides CO₂ is present. Based on these data, the monomer feed specification should be reviewed.”

Step 3: Develop a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible

In order to fully assess the possible causes of the upsets, the questions shown in Chapter 5 were utilized and Table 9-2 was developed.

The comments in Table 9-2 tended to confirm the suspicion that the upsets were caused by the presence of CO₂. However, there was still a residual doubt that possibly there was another impurity that was causing the problem. The problem solver determined that if the batch laboratory data could be shown to be consistent with plant data, this doubt would be removed. In order to develop this comparison, a technique was required to allow extrapolating short-term plant upset data to steady-state operations. The steady-state operation values would allow comparison to the batch laboratory data. After some literature research, the problem solver developed the four important concepts described in the next few paragraphs.

In most polymerization reactions, highly reactive impurities such as CO₂ react immediately upon entering the reactor. That is, the rate of catalyst

Table 9-2 Questions/comments for example Problem 9-2

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed.
Are all instruments correct?	The instruments had allegedly been calibrated. In addition, the heat balance was checked by manual calculations.
Are laboratory results correct?	Yes. The X-ray machine used to determine the catalyst concentration was cross-checked with another machine. No other impurities besides CO ₂ were observed on continuous analyzers during upsets. In addition, samples of the feed taken during upsets and analyzed in the laboratory confirmed the presence of CO ₂ .
Were there any errors made in the original design?	No.
Were there changes in operating conditions?	No.
Is fluid leakage occurring?	The potential for reaction quench fluids leaking into the reactor was checked and it was concluded that they were not leaking into the reactor.
Has there been mechanical wear that would explain the problem?	No.
Is the reaction rate as anticipated?	Yes, except during upsets.
Are there adverse reactions occurring?	Yes. During upsets the product quality attributes decreased.
Were there errors made in the construction?	Not applicable.

deactivation is not dependent on concentration of the impurity in the *reactor*, but depends on the concentration of the impurity in the *feed*. As discussed earlier, this is known as the “fast response model”. This is the first important concept.

The second concept is that for industrial problem solving, the polymerization reaction can be represented by simple first-order kinetics with respect to the catalyst and monomer concentration. The equation shown below was utilized to approximate the polymerization kinetics in a reactor with a fixed volume.

$$R = k * C * M \quad (9-10)$$

Where:

R = the polymerization rate or monomer consumption rate, lbs/hr

k = the kinetic rate constant including reactor volume, $\text{ft}^6/\text{hr-lbs}$

C = the catalyst concentration in the reactor, lbs/ft^3

M = the monomer concentration in the reactor, lbs/ft^3

Note that the units of the kinetic constant include a fixed reactor volume. The absolute value of the kinetic constant is not important since, as will be shown later, all that is considered is the relative change in this constant.

The third concept involves the modification of equation (9-1) to include a catalyst deactivation term and development of an expression for catalyst concentration in the reactor. The rate of accumulation of catalyst in the reactor can be expressed as shown in equation (9-11):

$$A_C = I_C - O_C - D_C \quad (9-11)$$

Where:

A_C = the rate of accumulation of catalyst in the reactor, lbs/hr

I_C = the inflow of catalyst, lbs/hr

O_C = the outflow of catalyst, lbs/hr

D_C = the deactivation of catalyst, lbs/hr

Based on the “fast response model”, any CO_2 entering the reactor will immediately deactivate some of the catalyst. This relationship can be expressed as follows:

$$D_C = Z * B \quad (9-12)$$

Where:

Z = the ratio of catalyst deactivated to CO_2 , lbs/lb

B = the rate of CO_2 entering reactor, lbs/hr

Equation (9-11) then becomes:

$$A_C = I_C - O_C - Z * B \quad (9-13)$$

If the flow of CO_2 continues for an extended period, steady state will be reached. At steady state, $A_C = 0$ and $O_C = I_C - Z * B$. This steady-state value will be the full impact of the particular rate of CO_2 entering reactor. While the deactivation ratio (Z) is of theoretical interest, it can be eliminated from pragmatic considerations as described later.

As indicated in equation (9-10), the important variable is the catalyst concentration in the reactor. Equation (9-13) can be transformed into equation (9-14) that uses the catalyst concentration by the appropriate substitutions.

$$dC/dt = (I_C - O_C - Z*B)/V \quad (9-14)$$

Where:

dC/dt = the rate of catalyst concentration change in lbs/ft³-hr

V = the volume of the reactor, ft³

Equation (9-15) can be used along with equation (9-14) and the initial catalyst concentration in the reactor to determine the concentration at any point in time.

$$C_i = C_0 - (dC/dt)*t \quad (9-15)$$

Where:

C_i = the catalyst concentration in the reactor at any point in time, lbs/ft³

C_0 = the original catalyst concentration in the reactor, lbs/ft³

t = the elapsed time from the start of the upset to C_i

The fourth concept involves developing a relationship between the concentration of active catalyst in the reactor at any point in time, the initial concentration and the final concentration. This relationship assumes that a step change is made to an equilibrium condition and that the step change is continued until steady state is reached.

This relationship will allow translating upset data into steady state for comparison to the batch laboratory data. For a perfectly mixed CSTR, the concentration of a component at any point in time after a step change is made can be expressed as shown in equation (9-16). In the specific case under consideration, the component is the catalyst and the step change is an increase in the CO₂ concentration in the feed.

$$(C_i - C_o)/(C_f - C_o) = 1 - e^{-T} \quad (9-16)$$

Where:

C_i = the concentration of catalyst in the reactor at any point in time

C_o = the concentration of catalyst in the reactor at time = 0

C_f = the concentration of catalyst in the reactor after an infinite amount of time

T = the number of reactor displacements. This is simply the time after a step change divided by the average residence time

As indicated in equation (9-12), the amount of catalyst deactivated by each pound of CO_2 is not known and was set equal to “Z”. However, the instantaneous reaction rate is directionally proportional to the catalyst concentration in the reactor (assuming a constant monomer concentration) regardless of the value of “Z”. Thus, the reaction rate can be substituted for the “C” values in equation (9-16). Equation (9-16) then becomes:

$$(R_i - R_o)/(R_f - R_o) = 1 - e^{-T} \quad (9-17)$$

Where:

R_i = the reactor production at any point in time

R_o = the reactor production at time = 0

R_f = the reactor production after an infinite amount of time

T = the number of reactor displacements at any point in time

Thus, if reactor production at time = 0 (R_o), the reactor production at any point in time (R_i), and the number of reactor displacements at any point in time (T) are known, the steady-state impact (R_f) of a step change in impurity level can be estimated. The number of reactor displacements is the time since the step change in impurity level occurred divided by the reactor residence time. The use of equation (9-17) also eliminates some of the concerns associated with theoretically imperfect derivation of equation (9-14) and equation (9-15).

Unfortunately, the impurity upsets observed by the problem solver did not occur as step changes. He simulated the approximate sinusoidal curve of concentration versus time that often occurred during upsets as a step change. A typical impurity curve along with the technique used to simulate a step change is shown in Figure 9-2.

The problem solver recognized that selecting the magnitude of the upset level to use was somewhat subjective. He tried to select it so that the areas below and above the increasing part of the actual curve were equal. He also used the peak in the concentration versus time curve as the termination point of the upset (R_i or C_i).

The problem solver used this four concepts technique because it provided a consistent method for evaluating upsets of varying magnitudes and durations. For example, an upset where the CO_2 concentration rose from 0 to 25 ppm and lasted for 15 minutes might have less actual impact than an upset where the CO_2 concentration rose from 0 to 5 ppm and lasted for 45 minutes. However, the projected steady-state impact of the first upset was greater. It was obvious that a steady-state concentration of 25 ppm of CO_2 in the monomer

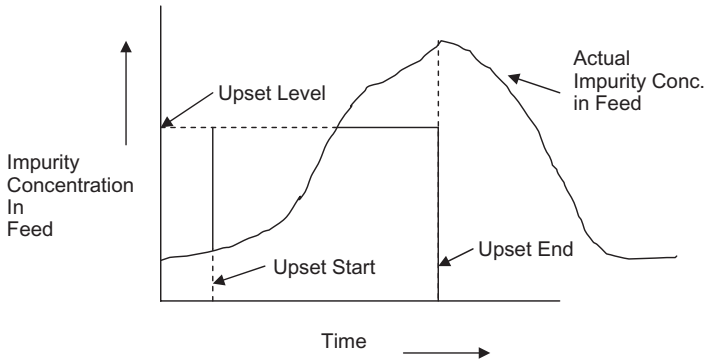


Figure 9-2 Simulation of actual change.

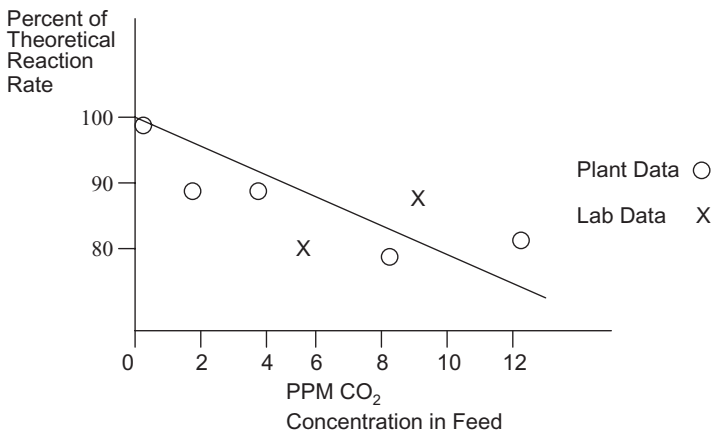


Figure 9-3 Projected steady-state reaction rate versus CO₂ concentration.

feed would have a much larger impact than 5 ppm. However, the exact magnitude of this difference could not be known without using the techniques described earlier.

In order to completely formulate the working hypothesis, several reaction upsets apparently caused by CO₂ of varying severity and duration were followed, and the techniques discussed above were used to extrapolate to the steady-state effect. These data along with the batch laboratory data are shown in Figure 9-3.

The problem solver then developed the following working hypothesis based on the data shown above:

“It is theorized that the short-term reaction upsets are due to the presence of CO₂ in the reactor feed. The plant data are consistent with laboratory data that indicates that CO₂ is a potent reactor impurity. The reaction upsets are likely to

cause product quality upsets due to the unsteady nature of the reactor during these transients. In addition, the presence of a potent reactor impurity is anticipated to affect polymer quality attributes. There were no indications of any other impurities in any of the upsets that were followed.”

Step 4: Provide a Mechanism to Test the Hypothesis

In order to test this hypothesis, a technique had to be developed to insure that the reactor feed was free of CO_2 for an extended period of time. If no reaction upsets occurred during this time period, agreement was reached that this would be considered a successful test and proof of the hypothesis. While it would involve additional operating cost, it was agreed to operate the monomer production facilities in a fashion that there would be minimal probability of CO_2 upsets. While this additional operating cost was not acceptable in the long range, it was acceptable for a 1-month trial. During this 1-month period, there was no measurable CO_2 present in the monomer feed nor were there any reaction upsets. Thus, this appeared to be a successful test and the working hypothesis was proven.

Step 5: *Recommend* Remedial Action to Eliminate the Problem without Creating Another Problem

Based on the successful test that proved the hypothesis, the following remedial actions were taken:

- An evaluation was made to determine if the specification should be reduced from the existing 10ppm to a lower level. Because of the high cost of the catalyst and the fact that operating at 10ppm would cause the reaction rate to decrease from 100 percent of theoretical to about 80 percent of theoretical (see Figure 9-3), it was concluded that the specification should be reduced to 1 ppm.
- Additional facilities were installed to allow reducing the specification from 10 to 1 ppm and to eliminate the occurrences of impurity upsets.
- A new highly accurate continuous analyzer to monitor the reactor feed for CO_2 was installed.
- Contingency plans were developed for the possibility of a CO_2 upset. These plans included shutting down the reactor if the concentration reached such a high level that serious product quality problems would be encountered.

9.7 LESSONS LEARNED

While this problem might be considered an isolated example that has minimal application to the industrial world, it should be recognized that upsets do

occur on a frequent basis. These upsets are often ignored because they are only short term. When they are considered, it is often with a minimal amount of data analysis and wrong conclusions are often reached.

In the real-life example problem, pursuing the presence of another impurity besides CO_2 would have been an easy trap to fall into because of the presence of previous experience and the persuasiveness of the proponent of the idea. However, it would have been the wrong route to pursue. It was only when data were developed and analyzed that it became obvious that the impurity upsets were associated with CO_2 . The problem also illustrates the value of quantitative data. The relationship between the concentration and reaction kinetics (Figure 9-3) allowed determination of the optimum monomer impurity specification.

The problem illustrates the type of shortcuts that can be taken in an industrial environment. While theoretically polymerization reaction kinetics involve several steps such as catalyst activation, polymerization initiation, polymerization propagation and polymerization termination, there is no need to include all of these reactions. Essentially all reactions can be modeled by simple first-order kinetics with respect to the catalyst and monomer concentration. In addition, since in this specific problem the reactor volume is fixed, there is minimal need to include it in the kinetic relationship. What is important is the model to be used for the reaction of the impurity (fast response or slow response) and the reactor fluid flow (CSTR or plug flow). In this case, the problem description includes the idea that the impurity CO_2 reacts immediately as it enters the reactor and thus can be simulated with a fast response model. The problem description also indicated that the reactor was a CSTR.

The fact that the impurity concentration versus time relationship was simulated as a step change was a decision made by the problem solver. It would have been possible to simulate this as a sinusoidal relationship. However, it is doubtful that this would have improved the accuracy of the solution and it would have increased the complexity of the approach significantly.

9.8 FINAL WORDS

The primary purpose of this chapter is to illustrate both the need to have and apply techniques for the unsteady state. The engineering concept given in equation (9-1) is simple.

$$AD = I - O - RD \quad (9-1)$$

The techniques required to apply the equation are much more complex. However, the problem solver must not be overcome by the complexity. Like all problems and/or projects, the complexity must be approached one step at a time. For example, what is the input, what is the output, and how can the reaction or addition or removal of heat be estimated. The benefit of doing the

work required to utilize the techniques described is that quantitative problem solutions are possible. For example in the first example (Problem 9-1), it was possible to specify the rate of reactant addition based on the data analysis.

The two example problems are actual problems. The time pressures to develop solutions rapidly were present. But there was also a need to work the problem right the first time as opposed to multiple “trial and error” attempts often characterized by the phrase “We have got to try something”.

Chapter 9 Table of nomenclature

A	The heat transfer area, ft^2
A_c	The rate of accumulation of catalyst in the reactor, lbs/hr
AC	The heat accumulation, BTU/hr
AD	Rate of accumulation. This could be accumulation of anything— level, heat or reactant
B	The rate of CO_2 entering reactor, lbs/hr
C	The catalyst concentration in the reactor, lbs/ft^3
C_f	The concentration of catalyst in the reactor after an infinite amount of time, lbs/ft^3
C_i	The catalyst concentration in the reactor at any point in time, lbs/ft^3
C_0	The original catalyst concentration in the reactor, lbs/ft^3
C_p	The average specific heat of material, $\text{BTU/lb} \cdot ^\circ\text{F}$
D_c	The deactivation of catalyst, lbs/hr
dC/dt	The rate of catalyst concentration change in $\text{lbs/ft}^3\text{-hr}$
dT/dt	The rate of temperature rise, $^\circ\text{F/hr}$
I	Inflow of material or heat
I_c	The inflow of catalyst, lbs/hr
k	The polymerization kinetic rate constant including reactor volume, $\text{ft}^6/\text{hr-lbs}$
M	The monomer concentration in the reactor, lbs/ft^3
O	Outflow of material or heat
O_c	The outflow of catalyst, lbs/hr
R	The rate of reaction. For the case of an instantaneous reaction, it is the rate of reactant addition, lbs/hr . For a polymerization reactor, it is the polymerization rate or monomer consumption rate, lbs/hr
R_f	The reactor production after an infinite amount of time
R_i	The reactor production at any point in time
R_0	The reactor production at time = 0

RD	Removal/addition of heat, or formation/destruction of material by reaction
T	The number of reactor displacements. This is simply the time after a step change divided by the average residence time
T_R	The temperature of the reactor, °F
T_C	The <i>minimum</i> temperature of the coolant, °F
t	The elapsed time from the start of the upset to C_i
U	The heat transfer coefficient, BTU/hr-°F-ft ²
V	The volume of the reactor, ft ³
W	The weight of material (metal, water, reactants), lbs
Z	The ratio of catalyst deactivated to CO ₂ , lbs/lb
ΔH_R	The heat of reaction, BTU/lb

VERIFICATION OF PROCESS INSTRUMENTATION DATA

10.1 INTRODUCTION

Data verification is a necessity of living for a successful problem solver. This is true whether the problem solver is working to discover a cure for cancer or working to get a process plant problem solved. In all cases, the verification involves *both* use of *human resources* and *technical resources*. While it may be possible to install multiple backup instrumentation, do frequent instrumentation calibrations and install elaborate communication devices to avoid the concept of data verification, this level of sophistication is rarely justified in a process plant.

Data verification can take many different approaches. The purpose of this chapter is to elucidate some of the techniques the author has developed and/or used that are beyond the conventional “check out the instrument” approach. The approaches discussed in this chapter are certainly not all inclusive. They are given for two purposes:

1. To illustrate some of the techniques that are available to check out suspect data. As technology growth occurs, newer techniques will cause this list to require continual updating.
2. To serve as an encouragement to the problem solver to take full responsibility for the area of data verification. Often the problem solver is tempted to quit and say “I can’t do any more until someone fixes the instrumentation.”

10.2 DATA VERIFICATION VIA TECHNICAL RESOURCES

The first step in verifying any instrument is a careful review of the instrument specification sheet and a comparison of the specification sheet to the actual field installation. The instrumentation specification sheet will have such information as instrument range, process fluid density, pressure and temperature. If these values are not correct or if the range or zero point is set wrong in the field, the data cannot be expected to be correct.

A second area to consider when reviewing the instrument specification sheet is actual operating conditions compared to design conditions. That is, how close is the variable being monitored to the design level of flow, pressure, level, etc.? Many instruments provide a measurement that is based on differential pressure. If the actual measured value is significantly different from the design level, there may be inaccuracy introduced by this deviation. This inaccuracy is often overlooked in the era of digital data acquisition where the measured variable may be shown in four or five “significant” figures regardless of what percent of the range this is. An analog picture that may help in understanding this involves measuring the pressure of an automobile tire. The absolute accuracy of a pressure gauge that is calibrated from 0 to 200 psig is much less than one that is calibrated from 0 to 40 psig. An error of 5 percent of maximum amounts to either 10 or 2 psig. This difference in accuracy is quite significant when measuring tire pressures of 30 psig.

This “percent of range” problem is particularly significant for an orifice flow instrument. With an orifice flowmeter, the differential pressure across the orifice is proportional to the rate squared. Thus, a flow rate of 50 percent of maximum design flow rate only provides an output of 25 percent of the full meter range. The meter accuracy at 25 percent of range will be much less than that at full meter range.

The concept of reviewing the instrument data sheet first, follows the idea of doing the easiest thing first. If errors are found or if the operating conditions are found to be only at a low percent of design conditions, these can almost always be rectified by simple adjustments of the instrument.

If the review of the instrument specification sheet fails to uncover any explanation for the suspected instrument being wrong, additional steps are required. In a continuous process plant, verification of instrumentation data is complicated by the fact that a shutdown of a process to verify an instrument is prohibitively expensive. Thus, data verification must be done by techniques that do not require a shutdown.

Essentially all instruments consist of both a primary element and a display element. The primary element senses a process variable such as pressure or differential pressure. The display element takes that reading and converts it to the variable being measured such as flow rate, pressure or level. The primary element is often not accessible without a partial or total plant shutdown. The display element can almost always be tested and replaced or adjusted while the process is in operation. For example, a flow instrument such

Table 10-1 Typical sources of primary element errors

Primary Element	Plugging in		Corrosion of Element	Condensation in Tubing
	Element	Tubing		
Flow	X	X	X	X
Level		X		X
Pressure	X	X		X
Differential pressure	X	X		X

X indicates that the primary element could likely be impacted by the condition shown at the top of the table.

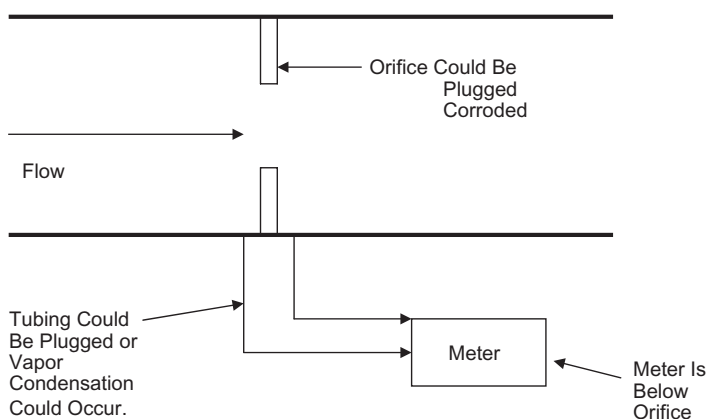


Figure 10-1 Potential flowmeter errors.

as an orifice meter both creates and measures pressure drop. Since the orifice plate which creates the pressure drop is installed in the flowing fluid, it cannot be removed from service without at least a partial shutdown. However, the display element can be checked and adjusted or replaced without a shutdown. The emphasis in this chapter is on data verification when the primary element is in question and cannot be removed from service.

Table 10-1 summarizes the typical sources of instrumentation errors of the primary elements. As an example of Table 10-1, the reader is referred to Figure 10-1, which shows a typical flow element and potential sources of errors.

As shown in Figure 10-1 and Table 10-1, the flowmeter can give erroneous results if one of the following occurs:

- The orifice could be partially plugged. This would create a greater than expected pressure drop for the given flow rate. This would result in the measured flow rate being higher than actual flow.

- The orifice could be corroded. This would create a lower than expected pressure drop for the given flow rate since the orifice hole would be bigger than the design. This would result in the measured flow being less than actual flow. If corrosion of an orifice plate does occur, it might result in an orifice hole that was not uniform or was very rough, which might well create greater than expected pressure drop and a measured flow being greater than the actual flow.
- One of the tubing lines leading to the display element could be partially plugged. This would give a pressure reading at the display element that was different than actual. The pressure sensors for the meter measure the pressure differential across the orifice. If the high-pressure side tubing is plugged, the measured pressure differential will be lower than actual. This will cause the measured flow rate to be less than actual flow. Conversely if the low-pressure side of the tubing is plugged, the differential pressure will be higher than actual and the measured flow rate will be higher than actual flow. Possible sources of plugging are solids in the process fluid or freezing of the fluid in the tubing lines.
- Condensation in the tubing lines can also create a false differential pressure. The comments here assume that the meter is located below the orifice so that condensation will accumulate in the tubing lines. If the meter is above the orifice, any condensation will normally drain back into the process flow by gravity. This condensation can occur when the orifice is in hot vapor service or the ambient temperature is colder than the temperature of the flowing vapor. If this condensation occurs in the high-pressure tubing line and not in the low-pressure tubing line, the measured differential pressure will be higher than that created by the pressure drop across the orifice. This will result in the measured flow being higher than actual flow. The converse is that if the low-pressure tubing line has more condensation than the high-pressure tubing line, the measured flow will be less than actual flow. If an equal amount of condensation occurs in both the high- and low-pressure tubing lines and the tubing lines have the same elevation change, then the impact on the measured variable is minimal. Since this is unlikely to occur in practice, the tubing lines are usually insulated and steam traced or sealed with either the process fluid or an instrumentation fluid that is not soluble in the process fluid. A similar situation can occur if the fluid is a liquid that can vaporize in the tubing lines.
- It is also possible for the flow measurement of a vapor stream entraining liquid droplets to experience a similar error. In this case, the liquid droplets may accumulate in one or both of the tubing lines. While these droplets may vaporize over time, this vaporization will be at a rate that depends on the ambient conditions. In addition, the rate of entrainment may also vary. Thus, there is no way to know that the tubing lines are full of liquid or vapor. The preventative steps described above are usually provided by the instrument designer in this case also.

Table 10-2 Data verification via technical resources

Type of Instrumentation	Repair Mode ⁽¹⁾	Data Verification Techniques
Flow measurement		
Primary element	Off-line	Insertable flowmeters, ultrasonic flowmeters, or process analysis
Display element	On-line	
Thermocouples with external wells		
Primary element	On-line	Thermometers, pyrometers
Display element	On-line	
Thermocouples without external wells		
Primary element	Off-line	Infrared pyrometers
Display element	On-line	
Pressure measurement		
Primary element with block valve	On-line	Pressure gauge
Display element	On-line	
Level measurement		
Primary element	Both off-line and on-line	Gauge glass, Geiger counter or X-ray
Display element	On-line	

(1) Off-line indicates that the process must be shut down to check or repair. On-line indicates that verification can be made while the process is in operation.

A similar description could be provided for each of the types of instrumentation measurements shown in Table 10-1.

Table 10-2 shows possible techniques for validating instrumentation data. The emphasis in this table is verification without requiring a plant downtime. Thus, the most obvious approach of replacing an “in-line” instrument is not covered. The following paragraphs discuss verification techniques for the most common instruments.

10.3 FLOW MEASUREMENT

If a primary flow measurement device (an orifice plate or venturi meter) is suspect and cannot be removed from service, it must be verified by either or both a noninvasive external flow measurement device or process analysis.

The external flow measurement devices are generally not as accurate as the flow measurement devices installed in the process. There are some claims for high accuracy. However, this is usually based on devices that have been calibrated against a known flow rate of the suspect process fluid. If this field calibration against a reliable flowmeter is not available, then the claims for high accuracy are questionable. In addition, some of the external measurement devices (pitot tube) require insertion through a bleeder valve with a packing gland arrangement. This packing gland arrangement creates some

Table 10-3 External flow measuring devices

Type of Device	Comments
Noninvasive ultrasonic instruments	These can be strapped onto a pipe and used to measure flow.
Transit time	Clean homogenous fluids. Accuracy has been reported from 10 to 70 percent.
Doppler shift	Used for suspended solids with concentrations from 200 ppm to the percent level.
Invasive	These require a bleeder and a packing gland arrangement to insert them into the flow.
Pitot tube	Can be highly accurate if sufficient readings are taken across the flow path and integrated to obtain the average flow. Generally for clean fluids only.

safety risk especially in high-pressure service. Table 10-3 lists a few of the external devices that are available. This is not meant to be an exhaustive list. In addition, the changing technology world may well allow development of different and/or more accurate devices.

Verification of a flow measurement by process analysis is a relatively simple, but often overlooked technique. It involves the use of heat and material balances to confirm the validity of a suspect flowmeter. It is probably best to consider it a “one-sided” test. For example, if the heat and/or material balances appear to check, the flowmeter is probably correct. If the heat and/or material balances do not check, the suspect flowmeter *or another* flowmeter is likely wrong. While these concepts are fundamental to all process engineering, some general guidelines are presented below to aid in the application of these principles:

- Accumulation may cause a system to appear to be out of material balance. Thus, it may be necessary to expand the traditional concept to utilize the principle of accumulation discussed previously in Chapter 9. That is,

$$AD = I - O - RD \tag{9-1}$$

Where:

- AD = rate of accumulation. This could be accumulation of anything—heat or material
- I = inflow of material or heat
- O = outflow of material or heat
- RD = removal of heat or material by reaction

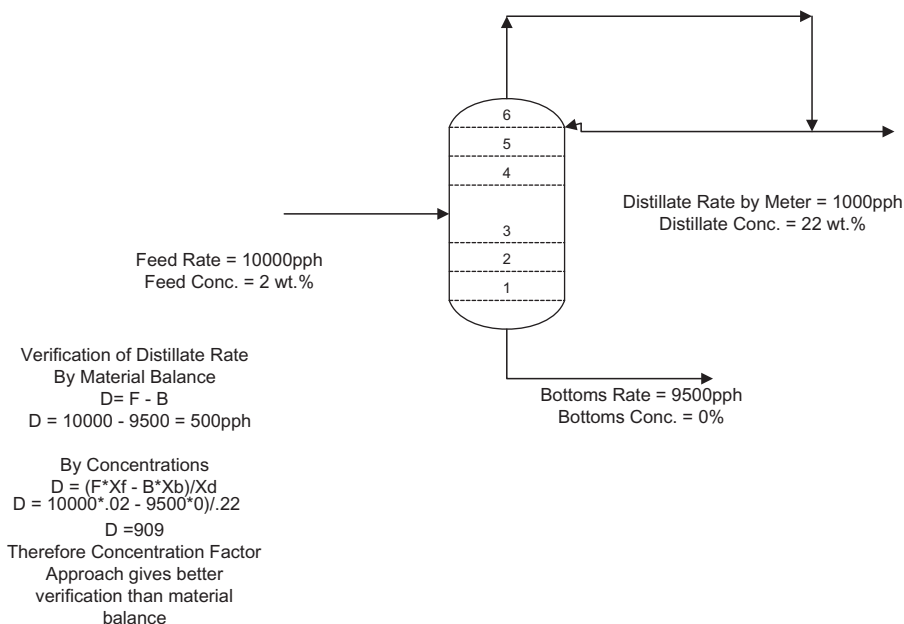


Figure 10-2 Estimating flow by concentrations.

- Beware of determining flow rate as the difference between two large metered flows. Using the concept of concentration factor provides more reliable answers. Figure 10-2 illustrates this point. As shown in this figure, if the overhead distillate rate is calculated as the difference between the feed rate and the bottoms rate, a value of 500 lbs/hr is obtained compared to a metered value of 1000 lbs/hr. However, if concentrations are used to estimate the overhead rate, a flow rate of 909 lbs/hr is calculated.
- Heat balances can be used to estimate the process or utilities flow to an operation. For example, the steam rate to a reboiler for a simple fractionation column can be estimated knowing that the heat added by the reboiler and feed must be equal to the heat removed by the process streams and cooling water. Other examples are, the cooling water flow to a tower condenser can be determined knowing the heat removed in the condenser and the inlet and outlet water temperatures; and the “boil up” rate in an evaporator can be determined by the steam rate and the heat of vaporization of the process fluid.

10.4 TEMPERATURE MEASUREMENT

Often a suspect primary temperature measuring element can be checked by removing it from a thermowell which is installed in the vessel or pipe. However,

in some instances, the primary device is not removable. An example of this is the tube metal thermocouples in a furnace. These devices are used to measure the temperature of the furnace tube metal. In order to obtain this measurement, the thermocouples are attached to the tube itself and shielded from the flame as opposed to being installed in a thermowell. This shielding ensures that the thermocouple does not receive any radiant heat from the furnace flames. A high tube metal reading could be real or associated with a failure of the device or shielding equipment.

In the case of furnace tube thermocouples that are suspect, infrared temperature measurement can be utilized to measure tube metal temperatures through a furnace porthole if it can be accessed safely. Infrared temperature measurement is a noninvasive technique to determine the temperature of a small area. It can be used to measure reasonably accurately the temperature of a particular spot on a furnace tube. It can also be used to measure the temperature of a flowing solid or to measure the temperature of a rotating part of machinery.

Infrared temperature measurement requires a great deal of expertise, particularly the measurement of furnace tube temperatures. For example, measurement of furnace tube temperatures may require that the infrared detector be cooled by liquid nitrogen.

10.5 PRESSURE MEASUREMENT

A suspect pressure instrument can many times be removed and a gauge installed to verify the pressure. However, if there is no way to isolate the pressure instrument or if the pressure tap is plugged, alternative methods of verifying the pressure instrument will be required. Fundamental process analysis can often be used to verify a pressure reading.

The classical chemistry phase rule can often be applied in this situation. This rule is as follows:

$$F = C - P + 2 \quad (10-1)$$

Where:

F = the degrees of freedom (temperature, pressure and composition)

C = the number of components in the mixture

P = the number of phases present

Thus for a single component system with two phases present, the degrees of freedom equal 1. This means if the temperature is known, the pressure is fixed. In a two-phase binary (two components) system, the degrees of freedom will be 2. If the binary system has a *fixed* composition, fixing the temperature

also fixes the pressure since the *fixed* composition eliminates one degree of freedom. While this may seem very basic chemistry/engineering, it is amazing how often this is overlooked in the data verification process. Example Problem 10-1 illustrates how this fundamental approach was used to solve a process problem rather than inventing more complicated theories.

10.6 LEVEL MEASUREMENT

The verification of a level instrument can often be done simply by utilization of a gauge glass if one is available. Other devices such as X-ray and Geiger counters can be used to determine the absolute level based on the fact that liquid is denser than vapor. Both of these techniques work in a similar fashion. A source of the radiation signal is located on one side of the vessel and a detector is located on the other side. The amount of radiation that reaches the detector is inversely proportional to the length of the flow path and the density of the material in the flow path. The material in the flow path includes both the vessel wall and the process fluids. Thus, if the radiation absorption of the metal wall can be eliminated by a calibration technique, the technique can detect the interface between liquid and vapor. Key factors in the use of either of these techniques are as follows:

- Difference in densities between the liquid and vapor. As the density difference decreases, it is more difficult to measure level with this technique.
- Thickness of the vessel wall. The thicker is the vessel wall, the more difficult it is for a signal to penetrate the wall of the vessel.
- Diameter of the vessel. At a fixed design pressure, larger-diameter vessels require thicker walls.
- Strength of the radiation signal. The stronger the source of the radiation signal, the easier it is to obtain a strong signal with the detector. However, stronger signals increase the radiation hazards and the design considerations difficulties.

Again process analysis can be used to verify the range of the level instrument. In order to verify the absolute accuracy of the level instrument, the zero point and range must be known. The zero point is the level in the vessel that corresponds to a zero reading on the level instrument. This may or may not correspond to an empty vessel condition. The range is the difference (usually in inches) between the zero point and the 100 percent indication of the vessel level. For example, a 6-foot-high vertical drum with a zero point set at the bottom tangent line of the vessel and a range of 72 inches would cover the entire height of the vessel. Thus, a reading of 50 percent on the level instrument would be expected to be 36 inches above the bottom tangent line.

If the vessel level instrument is in question, it may be due to an inaccurate zero point or an inaccurate range. The zero point and instrument range can often be checked without taking the vessel out of service. However, some types of level instruments cannot be checked without taking the vessel out of service. In addition, inaccuracies of level instruments can also be caused by internal vessel connection plugging.

If accurate flowmeters are available for the inlet and outlet flows, it may be possible to assess the accuracy of the range of the level instrument by accumulating in the drum or removing liquid from the drum and comparing the calculated inventory change from flowmeters to the measured inventory change. The approach to be used depends on the orientation of the drum. If the drum is a vertical vessel, the inlet and outlet flows should be set so that there is a significant difference between the two. The measured inventory change should then be compared to the calculated inventory change based on the flowmeters. If they compare well, this is a good indication that the range on the instrument is correct. However, the zero point could still be wrong. The zero point could be checked by reducing the inventory in the vessel until there was clear evidence that the drum was empty. The evidence could consist of “blowing through” as evidenced by the outlet flowmeter or by a change in temperature, which would indicate by the phase rule that there was only a single vapor phase present.

If the level instrument in question is on a horizontal vessel, the same technique can be utilized. However, determining the actual volumetric inventory change will be more difficult due to the curvature of the vessel walls. Tables and techniques are available to readily take this curvature into account. If an accumulation test is run with a horizontal vessel with a level zero point that is in error, it is possible to conclude that the level meter is correct due to the curvature of the drum. For example, a change in the level instrument from 65 to 70 (5 percent) might well be confirmed by the difference in flowmeters. However, if the actual level were 10 percent instead of 65 percent, a 5 percent level increase would seem in error when compared to the difference in flowmeters. To confirm the accuracy of the range of a level instrument on a horizontal vessel, it is best to run two tests at different vessel levels. If both of these tests indicate that based on differences in flowmeters the level changes appear correct, then it can be assumed that the range of the level instrument is correct. The techniques for determining the zero point discussed for a vertical vessel can also be utilized for a horizontal vessel.

10.7 DATA VERIFICATION VIA HUMAN RESOURCES

The role of the nonprofessional worker in problem specification was discussed earlier. It was implied that the operator or mechanic was cooperative and that all that was necessary was to solicit his data and/or the problem history. Obviously, an uncooperative worker can be a poor source of data by refusing to share his knowledge, presenting erroneous data or simply acting as a “smoke

screen”. For example, an instrument technician that was known to have acrophobia probably did not check out an instrument as he claimed if it required him to be far above the ground.

While this book does not cover all aspects of interpersonal skills, the guidelines below will help the problem solver obtain the maximum assistance from the operating and mechanical workers.

- Respect the person that you are seeking information from as an equal whether he is college educated or not.
- Learn people’s names and don’t forget them.
- Cultivate relationships by providing answers to questions, explaining your goals, reviewing the results of any tests and listening to other’s thoughts.
- Don’t give the nonprofessional workers the impression that you are too busy to spend time with them.
- Be positive. Assume that people are always trying to do the right things. If a mistake has been made, assume that it was due to inadequate training or done accidentally. Don’t take the position that someone did it on purpose. You will be wrong on occasions, but you won’t destroy relationships.
- When it is occasionally necessary to look over someone’s shoulder as they perform their job, try to convince them that they are educating you on their skills.
- Realize that everyone has bad days. If you get an undeserved “chewing out ” by an operating or mechanical worker, take your licks and back away from the conversation without becoming defensive. Defending yourself to someone that is irrational is not possible and you will cut off a source of future data.

10.8 EXAMPLE PROBLEMS

The example problems below illustrate some of the approaches described in this chapter. The first problem is a real-life problem that illustrates the value of investigating and verifying conflicting data as opposed to simply assuming that one piece of the mysterious data is wrong. The second problem is a real-life problem that was solved by a careful review of the instrumentation specification sheet. The third problem is a fictitious problem that is included to illustrate how the technique of inventory change can be used to confirm a level instrument.

10.9 EXAMPLE PROBLEM 10-1

A vessel in an ethylene refrigeration unit shown in Figure 10-3, served as a combination surge and knockout drum. Liquid ethylene flowed into the drum

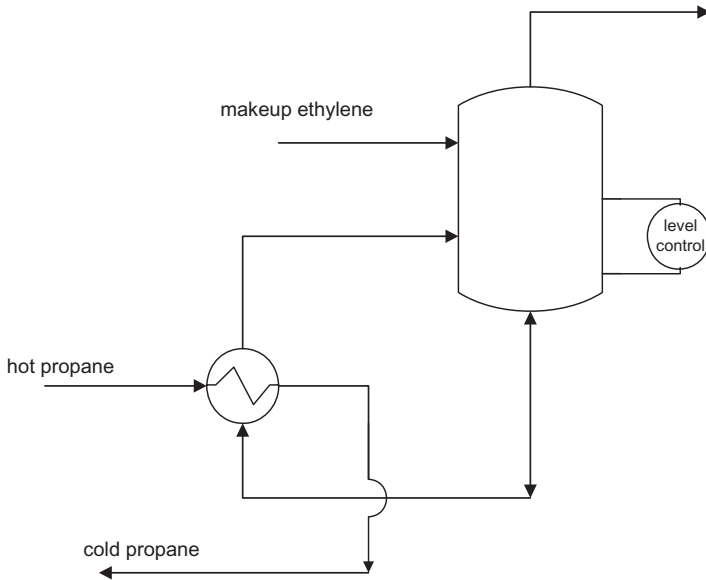


Figure 10-3 Ethylene surge/knockout drum.

and flowed out to various heat exchangers. The mixture of vapor and liquid ethylene leaving the exchangers was returned to the drum where it was separated into vapor and liquid streams. The ethylene refrigeration system was used to cool liquid propane to a temperature of -145°F . It was important to control the liquid level in the drum to insure that minimal amounts of liquid were entrained with the vapor and also to insure that liquid ethylene was always available for feeding the heat exchangers. The drum operated under a slight vacuum and the normal temperature was -156°F .

Current conditions were an anomaly. The pressure was at normal conditions. This slight vacuum was confirmed by a second independent pressure instrument. However, the temperature as measured by two independent thermocouples was $+10^{\circ}\text{F}$. Operating personnel believed that the thermocouples were both wrong. Management had asked that technical resources determine what the real problem was.

The problem solver's approach to using the five-step problem-solving technique was as follows.

Step 1: Verify that the Problem Actually Occurred

Since there were two independent thermocouples that both indicated a much higher than expected temperature, it was obvious that something was wrong. This was a real problem.

Step 2: Write Out an *Accurate Statement of What Problem You Are Trying to Solve*

The problem statement that was developed was:

“The temperature on the ethylene knockout drum is reading much higher than normal. While the process appears to be operating normally, this higher temperature may be indicative of a potential problem that will occur in the future. Determine why the temperature on the ethylene knockout drum is reading much higher than the normal temperature of -156°F .”

Step 3: *Develop a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible*

Using the questions from Chapter 5, the problem solver developed Table 10-4.

Based on the questions, four hypotheses were developed as follows:

1. There is a leak in the exchanger and the drum contains a mixture of propane and ethylene instead of pure ethylene.

Table 10-4 Questions/comments for Problem 10-1

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed.
Are all instruments correct?	The instruments had allegedly been calibrated.
Are laboratory results correct?	Not applicable.
Were there any errors made in the original design?	No. The process was an old one that was returning to service after repairs.
Were there changes in operating conditions?	No.
Is fluid leakage occurring?	The propane being cooled could leak into the ethylene refrigerant and concentrate in the knockout drum.
Has there been mechanical wear that would explain the problem?	The unit had been down for repairs. The repairing of the insulation on the drum might not have been completed.
Is the reaction rate as anticipated?	Not applicable.
Are there adverse reactions occurring?	Not applicable.
Were there errors made in the construction?	See comments above on mechanical wear. In addition, new thermocouples were installed.

2. The thermowell is so poorly insulated that the temperature instrument is really reading a mixture of the ethylene and the ambient temperature.
3. The new thermocouples were calibrated incorrectly.
4. The level instrument is wrong and there is no liquid level in the drum.

Hypothesis 2 was ruled out by an inspection of the drum that showed the thermowells were well insulated. Hypothesis 3 was ruled out after discussions about the calibration techniques used by the instrument technicians.

The problem solver used the phase rule (equation (10-1)) shown below to conclude that either hypothesis 1 or 4 were theoretically correct working hypotheses.

$$F = C - P + 2 \quad (10-1)$$

Based on the phase rule, he outlined the following three cases:

1. Under normal situations in the ethylene surge drum, there would be a single component ($C = 1$), two phases ($P = 2$), and the degrees of freedom (F) would be equal to one. That is, the temperature in the surge drum would be fixed by the pressure and should be -156°F .
2. If there were two components ($C = 2$) in the drum, then the degrees of freedom would increase to 2 and the temperature and pressure in the drum would be independent.
3. If there were a single component in the drum ($C = 1$) but only a single phase ($P = 1$), then the degrees of freedom would also be equal to 2. Again the temperature and pressure in the drum would be independent.

However, there are boundaries to this independence of temperature and pressure in case 2 shown above. For example, if there are two phases present and an exchanger leak had occurred (hypothesis 1), the temperature in the drum cannot be warmer than the boiling point of propane. If the liquid level instrument is correct (two phases are present) and as an extreme case all of the liquid in the drum is propane, the following analysis could be made:

$C = 1$ (Nothing in the drum, but propane.)

$P = 2$ (The level instrument is correct so there must be two phases.)

Therefore:

$$F = 1 - 2 + 2 = 1 \quad (10-2)$$

The boiling point of propane at atmospheric pressure is -44°F . Thus, even if the liquid in the drum were 100 percent propane, the temperature would be slightly below -44°F not $+10^{\circ}\text{F}$.

As discussed in case 3, if there was no leak in the exchanger, but the level instrument was wrong and the drum was empty (hypothesis 4), the phase rule would indicate the following:

$C = 1$ (Nothing in the drum but ethylene.)

$P = 1$ (Nothing in the drum but vapor.)

Then:

$$F = 1 - 1 + 2 = 2 \quad (10-3)$$

In this case, the temperature of the ethylene vapor would be limited only by the amount of superheat added by the heat exchangers.

Therefore, the theoretically sound working hypothesis developed was as follows:

“It is theorized that the mysterious temperatures in the ethylene knockout drum are due to the absence of a liquid level in the drum. Since there is no liquid level in the drum, the vapor can be heated to temperatures above the boiling point of ethylene at the pressure in the drum. In addition, the absence of this boiling liquid results in a very low heat transfer coefficient between the phase in the drum (vapor) and the thermowell. The normal situation in the drum is such that the thermowells are covered with boiling ethylene. The heat transfer coefficient in the normal case is likely as high as $200 \text{ BTU/hr}\cdot^{\circ}\text{F}\cdot\text{ft}^2$. The heat transfer coefficient from vapor to the thermowell is likely as low as $10 \text{ BTU/hr}\cdot^{\circ}\text{F}\cdot\text{ft}^2$. With this exceptionally low coefficient, the heat gained from the atmosphere flowing through the insulation and heating the thermocouple may create an additional error source.”

Step 4: Provide a Mechanism to Test the Hypothesis

While the hypothesis could have been checked by simply raising the liquid level in the drum, this was deemed too risky. Since the drum served as a knockout drum, there was a risk of a high level causing liquid ethylene to be carried over into the compressors. The problem solver requested that the instrument technician (who had recently checked the level instrument and determined that the range and zero point were as they should be) accompany him to again check the instrument. He explained to the instrument technician why he thought that the level instrument was incorrect. When they jointly inspected the installation, they found that the steam tracing that was used to insure that there was no liquid accumulation in the tubing lines was turned off. When this tracing was returned to service, the level instrument began to function correctly.

Step 5: *Recommend Remedial Action to Eliminate the Problem without Creating Another Problem*

In this case, the mechanism to test the hypothesis was the remedial action. In order to prevent future occurrences of this problem, a statement was added to the start-up procedure that called for the operators to check that the steam tracing had been put into service.

10.10 LESSONS LEARNED

While it is true that an experienced engineer would not need to use the phase rule to analyze this problem, that is only because he knows by experience and intuition how to analyze similar situations. In applying his experience and intuition, he is using the phase rule whether he knows it or not. This problem might be considered too simple for an engineering analysis; however, it does illustrate two important points. In the first place, there is great value in doing a fundamental analysis instead of making the assumption that the first analysis (the thermocouples are both wrong) is correct. It would be unlikely that both thermocouples were incorrect unless there was an external circumstance such as they were incorrectly calibrated or the heat transfer to the thermocouple was not what it should have been. As indicated, this could be due to excessive heat loss from the thermowell due to poor insulation or poor heat transfer (caused by the absence of liquid) from the vessel contents to the thermowell. The application of the phase rule was very helpful in indicating that the level instrument, which had been checked out, was truly in error.

The problem also indicates that it is often necessary to get an operator or mechanical personnel to recheck something that has already allegedly been checked. This requires tactfulness and a good working relationship. This good working relationship is developed by the principles indicated in Section 10.7. In this example problem, it was enhanced by the problem solver going with the instrument technician to look at the level instrument for a second time.

10.11 EXAMPLE PROBLEM 10-2

A new polymer was to be produced in a test run in a commercial polypropylene plant. This new polymer was to be a copolymer produced by using ethylene as a comonomer in reactors normally polymerizing only propylene. Careful preparations were made for the test run including reviews of batch and pilot plant operations producing the copolymer. These data indicated that the ethylene conversion should be about 85 percent during the planned operation. The test run plans called for careful monitoring of all variables especially the ethylene conversion. The ethylene conversion was to be monitored using the propylene and ethylene flowmeters, the ethylene content of the polymer and

the ethylene content of the unreacted gases. Because of the reliance on feed flowmeters, these were carefully checked out by the instrument technicians prior to beginning operation.

After the test run was started and steady state was established, the calculated ethylene conversion based on flowmeters and the ethylene content of the polymer was essentially 100 percent. This was in contrast to the ethylene content of the unreacted gases which indicated that the ethylene conversion was significantly less than 100 percent. While the unit ran well, the problem solver was greatly concerned about the deviation from the anticipated conversion based on calculations made using the feed meters. He convinced management that even though this discrepancy between the anticipated conversion and the apparent actual conversion did not seem to be a problem on this run, that it might be a problem on future runs. They agreed that he should spend some time investigating the problem.

The problem solver's approach to using the five-step problem solving technique was as follows.

Step 1: Verify that the Problem Actually Occurred

Since the test run had been carefully planned and the instruments checked out ahead of time, there was no doubt that there was a problem. There was some doubt about whether the problem merited attention. The problem statement developed by the problem solver had to address the incentive for working the problem.

Step 2: Write Out an *Accurate* Statement of What Problem You Are Trying to Solve

The problem statement that was developed was:

“The calculated ethylene conversion based on the ethylene feed flowmeters and the ethylene content of the polymer is about 100 percent. This is in conflict with the pilot plant data and also in conflict with the analysis of the unreacted gases which shows the presence of ethylene. If the flowmeters are correct, then either the ethylene content of the polymer or the ethylene content of the unreacted gases is wrong. The process control strategy requires that all three variables (feed flowmeters, ethylene content of the polymer and ethylene content of the unreacted gases) be measured correctly. Determine why the ethylene conversion is significantly higher than anticipated based on feed flowmeters.”

Step 3: Develop a Theoretically Sound Working Hypothesis that Explains as Many Specifications of the Problem as Possible

Using the questions from Chapter 5, the problem solver developed Table 10-5.

Table 10-5 Questions/comments for Problem 10-2

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed.
Are all instruments correct?	The instruments had allegedly been calibrated. The ethylene flowmeters and the analyzer for measuring the ethylene content of the unreacted gases were being used for the first time.
Are laboratory results correct?	The technique for measuring the ethylene content of the polymer had been closely cross-checked against known standards.
Were there any errors made in original design?	Since this was the first time that the ethylene meters and analyzers had been used, their design could be in error.
Were there changes in operating conditions?	Not applicable.
Is fluid leakage occurring?	Not applicable.
Has there been mechanical wear that would explain the problem?	Not applicable.
Is the reaction rate as anticipated?	Higher than anticipated ethylene conversion might explain the apparent discrepancies.
Are there adverse reactions occurring?	Adverse reactions are highly unlikely.
Were there errors made in the construction?	Since both the ethylene flowmeters and the ethylene analyzer were being used for the first time, this had to be considered.

Based on the above questions, four hypotheses were developed as follows:

1. There was a design mistake in sizing the ethylene flowmeters.
2. There was an error made in the installation of the ethylene flowmeters.
3. The unreacted gas analyzer had been incorrectly calibrated for ethylene. Or else the installation or design of the analyzer made it unacceptable for ethylene monitoring.
4. The technique for analyzing for ethylene in the polymer was either incorrect or being done incorrectly.

While any of the four hypotheses could be selected as a “theoretically sound working hypothesis”, the problem solver elected to do some further investigation prior to proposing a working hypothesis. Since the easiest and quickest thing to do was to review the instrument specification sheets, he

Table 10-6 Specification and actual data

Variable	Specification Sheet	Actual Data
Pressure, psig	735	735
Temperature, °F	90	75
Critical pressure, psig	735	735
Critical temperature, °F	50	50
Compressibility (Z)	1.0	0.6
Density, lbs/ft ³	3.56	6.10

elected this route. In addition, he recognized that the pretest instrument check by the instrument technicians did not involve a review of the instrument specification sheet. A review of the specification sheet indicated the values shown in Table 10-6.

The original instrumentation design used a density that was significantly less than the actual density because the gas compressibility that occurs at high pressures was not considered. There was also a difference in actual and design temperatures, but this was not significant. These calculations led to the following theoretically sound working hypothesis:

“It is theorized that the discrepancies between the actual ethylene conversions and the indicated ethylene conversions are due to the fact that the density for the ethylene flowmeters was calculated assuming that the compressibility was 1. This resulted in a calculated density that is 40 percent below actual density. Since the measured flow rate is directly proportional to the square root of the density, this error results in a measured flow rate that is 30 percent below the actual flow rate. This single error explains the discrepancies observed.”

Step 4: Provide a Mechanism to Test the Hypothesis

The mechanism for testing the hypothesis was very simple. Since the error was in the calculations, it was easily corrected by changing the range on the flow instrument to correct for the incorrect density. After this correction was made, the flow rates, ethylene content of the unreacted gases, and ethylene content of the polymer were all consistent with the anticipated results.

Step 5: *Recommend* Remedial Action to Eliminate the Problem without Creating Another Problem

In this case, the testing mechanism was the permanent solution. It should be noted that in this problem, there was a temptation to simply modify the process control computer with a fudge factor to adjust for the error. This was easy to do, but it brought with it the risk that at some future time, the factor that was used in the computer would be removed because someone did not

understand what it was. It was much more “fool proof” to change the instrument range and revise the instrument specification sheet.

10.12 LESSONS LEARNED

It should be noted that the error in the instrument specification sheet was only discovered after the problem solver realized that the pretest instrument check-out done by the instrument technicians only included a physical check of the instruments against the range given on the instrument specification sheet. They had no way of knowing that the density used in calculating this range was incorrect. The problem-solving lesson to be learned is that the problem solver needs to know the boundaries of the mechanics or operators when they are asked to check out a piece of equipment. If they are starting with an incorrect calculated setting, they can only confirm that the instrument or piece of equipment is set to that value.

While it could be argued that the effort to resolve this discrepancy was not justified, the discrepancy was a particular concern since the flowmeters were a key to changing grades. In addition, some grades produced at high ethylene contents could cause process shutdowns if control were lost. As a general rule, discrepancies in data or things that we do not understand will almost always cause future problems.

This example problem also illustrates again the value of doing the easiest calculation or data review first. While it seemed hard to believe that the design team would ignore the compressible nature of ethylene at high pressures, the simple review of the instrument specification sheet showed that this indeed was the case. Other hypotheses described earlier would have been more involved and taken longer to pursue.

10.13 EXAMPLE PROBLEM 10-3

This problem is included to show the calculation technique discussed earlier. The five-step problem-solving approach is not considered. In addition, the tables that show liquid volume as a function of level in a horizontal drum are not included. For simplicity, the head volume of the drum is not included. In order to illustrate the calculation technique, it is assumed that the bottom connection of the differential pressure type level indicator is partially plugged so that the indicated level is 15 percent greater than the actual level.

A pump taking suction from a horizontal vessel continued to experience intermittent periods of operating below the pump curve. At times, it operated well. After an extensive problem-solving analysis, it appeared that the level instrument was incorrect. The level instrument was checked by instrument technicians and the range and zero point appeared to be correct. The problem solver decided that the only way to confirm the accuracy of the level instru-

Table 10-7 Summary of test basis

Drum Size	
Diameter, feet	10
Length, feet	30
Fluid density, lbs/ft ³	30.6
Inlet flow—outlet flow, lbs/hr	10000
Test time, minutes	30
Volumetric flow, ft ³	163.3

Table 10-8 Test run results

	Test 1	Test 2
At test start		
Indicated level ⁽¹⁾ , percent	25	65
Actual level, percent	10	50
Actual contained volume, ft ³	123	1178
At test completion		
Actual contained volume, ft ³	286	1341
Actual level, percent	17.9	55.5
Actual level change, percent	7.9	5.5
Measured level change, percent	6.1	5.8
Error, percent	23	5

(1) The problem description indicated that the level instrument showed 15 percent higher than the actual level.

ment was with a plant test using the inlet and outlet flowmeters. He planned to use the flowmeters to calculate the level change in the drum. He would then compare this change to the measured change to try to determine if the level instrument was correct.

A summary of the test is shown in Tables 10-7 and 10-8.

An examination of Table 10-8 indicates the risk of running an accumulation test at only one level. If the test is run at a starting indicated level of 65 percent, it would be easy to conclude that the actual level change and calculated level change were very close. However, if the test run were started at an indicated level of 25 percent, the conclusion would be that there is a significant difference between the actual level change and calculated level change.

Chapter 10 Table of nomenclature

- F The degrees of freedom (temperature, pressure and composition)
- C The number of components in the mixture
- P The number of phases present

SUCCESSFUL PLANT TESTS

11.1 INTRODUCTION

Step 4 of the five-step problem-solving procedure often involves a plant test of some kind. These tests can vary from very straightforward to very complicated. While some of these comments were included in Chapter 3, conducting a successful plant test is so important to solving many problems that it deserves a separate chapter.

As indicated earlier, a successful plant test is one that either confirms the hypothesis is correct or proves that the hypothesis is not correct. An unsuccessful plant test is one that fails to either confirm or negate the hypothesis. In addition, it is important that the plant test be conducted in such a fashion that it does not create a major plant operating problem. The concept of analyzing problem solutions for potential problems was discussed earlier. Before conducting any plant test, a well thought-out potential problem analysis should be completed.

The Russian nuclear power plant disaster at Chernobyl was at least partially due to failure to complete a well thought-out potential problem analysis ahead of the test. The test was designed to determine whether, in the event of a reactor shutdown, enough power to operate the emergency equipment and core cooling pumps until the diesel power supply came online was available. It was to be conducted during the planned shutdown of reactor 4. The following contributed to the disaster:

- Only six to eight control rods were used during the test despite there being a standard order stating that a minimum of 30 rods were required to maintain control.
- The reactor's emergency cooling system was disabled.
- The test was carried out without a proper exchange of information between the team in charge of the test and personnel responsible for the operation of the nuclear reactor.

11.2 INGREDIENTS FOR SUCCESSFUL PLANT TESTS

All successful plant tests will require the following:

- A full evaluation of instruments and laboratory procedures to be used for the test.
- A careful statement of what results are anticipated and how the anticipated results will be evaluated. This will almost always involve a significant amount of pretest calculations.
- A complete well thought-out potential problem analysis including "trigger points" which, if violated, will cause the test to be terminated.
- A careful and detailed explanation to operating personnel about the test.
- A formal post-test evaluation and documentation.

These items are discussed in more detail in the following paragraphs.

11.3 PRETEST INSTRUMENT AND LABORATORY PROCEDURE EVALUATION

One might think of an evaluation of instrumentation prior to a plant test of involving only instrument technicians "zeroing" and calibrating instruments. In addition, the instrument specification sheets themselves should be reviewed if there is any doubt at all about the instrument validity. For example, as discussed in Chapter 10, during a plant test in a high-pressure process, it was difficult to get a good material balance using instrumentation. All instrumentation was checked and confirmed to be as indicated on the specification sheets. On a closer evaluation of the specification sheets, it was discovered that no allowance had been made for gas compressibility at the high pressures. This would result in a higher density than that calculated using the ideal gas relationships. There will probably be value in reviewing the specification sheets of all new instruments to be used in a plant test.

While laboratory procedures may be thought of as the domain of the chemists, if things do not appear to make logical sense, the problem solver should

not assume that the procedure is correct or is being correctly followed. As an example, during a start-up of a chloride removal system, strange laboratory results were being reported. The procedure developed to test for the level of the chloride ion called for acidification of the sample prior to running the test for chlorides. The laboratory technician used his most available acid (hydrochloric acid) for the acidification step. This was discovered only when a *tactful* process engineer asked if he could watch the laboratory technician perform the test. Upon a careful examination of the procedure, a footnote was found that indicated that nitric acid should be used in the acidification step.

These two examples are provided to indicate how the process engineer or problem solver must be involved in every step of the problem-solving efforts and/or plant test preparations regardless of the discipline that has primary responsibility. In these two cases, a more thorough review of things prior to the plant tests would have allowed discovering that the incorrect gas compressibility was used as the basis for flowmeter calculations and that the laboratory procedure was not as clear as it should have been.

11.4 STATEMENT OF ANTICIPATED RESULTS

Essentially all plant tests are directed at improving plant operations. However, in order to obtain an adequate evaluation of the plant test, it is imperative that the anticipated results be stated as quantitatively as possible. In addition, the variable or variables to be used to monitor the results of the plant test should be quantified. Both the positive and potential negative results should be spelled out. For example, a plant test on operating a fractionation column at a 15 percent increase in reflux rate to improve the purity of the distillate might have anticipated results stated as:

“It is expected that this plant test will provide an increase in distillate purity of 0.5 weight percent. The distillate purity will be measured by the standard laboratory test procedure which is accurate to within 0.1 weight percent. An increase in tower pressure drop of 0.5psi with no indication of tower flooding is anticipated. Tower flooding will be monitored by deviations from anticipated values of tray efficiency, tower pressure drop and heat balance closure.”

There are several things to notice in this statement. The fact that these are anticipated results means that calculations have been performed to determine the impact of the increase in reflux rate. For these calculations to be meaningful, similar calculations must be performed on the “base case”. That is, fractionation calculations should be performed for the normal operating conditions. These fractionation calculations are based on theoretical trays. The base case tray efficiency can be determined by varying the number of theoretical trays in the calculations until the calculated compositions match the laboratory results. At this point, the tray efficiency can be determined by dividing the

number of theoretical trays by the actual number of trays. This same tray efficiency can be utilized to estimate the change in distillate purity with the increased reflux rate.

If the anticipated distillate purity were not obtained, it would be an indication that the tray efficiency has decreased. This could be the result of some kind of tray overloading condition. In a like fashion, the tower heat balance closure can be determined for the “base case”. Heat balance closure is the difference between the heat added including all heat sources (feeds and external heat source) and the heat removed with the products and cooling sources. In theory this value should be zero. However, it is rarely zero due to meter errors and heat losses. If the heat balance closure becomes worse as the reflux is increased, it is likely due to tower flooding. Tower flooding *can* cause liquid to be entrained from the top of the tower into the reflux accumulator. The heat balance calculations assume that anything that enters the reflux accumulator came out of the tower as vapor. If some of the material going to the reflux accumulator is in fact liquid entrainment, the heat balance calculations will show more heat being removed from the condenser than is the actual case. This will result in a change in heat balance closure.

The fact that an anticipated tower pressure drop increase of 0.5 psi is indicated means that tray pressure drops have been calculated. The value in doing tray pressure drop calculations is twofold. It is necessary in order to assess whether tray flooding at the higher reflux rates would be anticipated. In addition, it provides an anticipated pressure drop which can serve as a “trigger point” to abort the test if it is exceeded.

In addition to the pretest calculations, the anticipated results include a statement about the accuracy of the laboratory test. A plant test where the anticipated distillate purity increase is 0.5 weight percent would be meaningless if the laboratory accuracy was only ± 0.5 weight percent.

The example of a fractionation column is very straightforward and easy to quantify with both statements and calculations. A more difficult plant test might be one in which a new catalyst with anticipated higher reactivity was to be tested. A similar technique to that described in Chapter 8 could be utilized to determine the actual higher reactivity of the new catalyst. The simplified kinetic constant of the “base case” catalyst could be determined knowing the reactor residence time and the reactant concentrations. The simplified kinetic constant for the new catalyst could be determined using the same variables. The comparison of these two kinetic constants could be made to determine the increased reactivity of the new catalyst. While this is more involved than the less rigorous method of just comparing catalyst efficiencies (pounds of product produced per pound of catalyst), it avoids the need for the plant test to be run at the exact same residence time and reactant concentration. Plant tests of new high reactivity catalysts are often conducted at lower feed rate, production rate and/or reactant concentration to avoid potential problems that might be associated with the higher reactivity. Catalyst efficiency will be impacted by these changes. Thus, a comparison based on catalyst efficiency

only will not be valid. This type of more complex plant test often involves considerations that on the surface seem difficult to assess. Many times it is possible to assess these considerations using fundamental chemical engineering skills. Two example problems are discussed later.

11.5 POTENTIAL PROBLEM ANALYSIS

A complete well thought-out potential problem analysis is mandatory. A “trigger point” should be developed for each major potential problem. If these “trigger points” are violated, the test will be terminated. Most of the variables considered in the statement of anticipated results will be considered in the potential problem analysis. While the concept of potential problem analysis is closely related to the previous discussion, there are some additional considerations. Some of these are related to safety. While the list below is not an all-inclusive list, it is a list of the type of safety-related questions that should be considered:

1. Are any new chemicals being used?
2. Have by-product reactions and byproducts been evaluated?
3. Are any new chemicals or reaction by-products compatible with the existing materials of construction?
4. Are the test operating conditions outside acceptable ranges?
5. Are there any proposed conditions that will cause the safety release systems to be inadequate? For example, a higher reactivity catalyst might cause safety release facilities to be undersized.
6. Will operating condition changes cause a highly reactive chemical to concentrate to an unsafe level or be at unsafe conditions? Some examples are:
 - Oxygen concentrating in a vent to the point that the oxygen–hydrocarbon mixture is in the explosive range.
 - Operating conditions for systems handling ethylene or acetylene reaching a pressure and/or temperature that can result in thermal decomposition.
 - Operating temperatures for a thermally sensitive polymer being so high that decomposition with release of highly reactive monomers occurs.
7. Are there changes in operating conditions which seem innocuous but could, along with a single unexpected occurrence such as a utility or mechanical failure, lead to catastrophic results?

The above list as indicated is not inclusive, but is only to serve as example of the type of safety items that should be considered. Any list of this type must

not be considered a “checklist”. But it should be considered as a guideline only. “Checklists” often have a way of defeating their purpose by allowing the person responsible to simply check off items. In the pretest work for a plant test, serious consideration and likely significant calculations should be completed to insure that no safety-related problems will occur.

In addition to safety-related items, an analysis should be made of what kind of things could go wrong (potential problems) during the plant test. As indicated earlier, each potential problem should have a “trigger point”. If this trigger point is violated, the plant test will be terminated. The value of having pretest trigger points is that they can be calculation based when time is available for careful planning. This is opposed to waiting until unexpected events occur during the plant test and intuition becomes the mode of decision making. Examples of these trigger points are:

1. A new catalyst introduced into the reactor might lead to fouling of the heat transfer surface. In this example, the trigger point should be heat transfer coefficient. A trigger point of reactor temperature only will not be sufficient to determine if the heat transfer surface is fouling. The trigger point for the heat transfer coefficient should be set high enough to avoid the possibility that a small increase in catalyst rate will cause an uncontrolled increase in reactor temperature. Chapter 4 discussed a real-life example of this type of event.
2. A change in the reflux rate to a distillation column that should lead to an increased purity should include a trigger point to allow monitoring of unexpected tray performance deterioration. One possibility would be a trigger point specification on column pressure drop. The anticipated effect on column pressure drop could be calculated prior to the test and monitored during the test.
3. A plant test on adding a reagent to an exothermic batch reaction at a rapid rate might be monitored by a trigger point of temperature increase in the initial 2 or 3 minutes of reagent addition. Calculations prior to the test could determine the maximum temperature increase to avoid exceeding the maximum desired reactor temperature. If this calculated initial value was exceeded, the test would be terminated. Chapter 9 includes an example of this type of trigger point monitoring.

Hypothesis testing in a commercial plant may involve using results based on laboratory or pilot plant studies. Sometimes these results are based on equipment that does not simulate the commercial process exactly. A potential problem analysis should include possibilities associated with differences in equipment such as:

1. Did the reactor used in the studies simulate the commercial facilities?
Considerations must be given to:

- Simulation of a continuous reactor with a batch reactor.
 - Differences in mixing patterns and regimes in a laboratory or pilot plant reactor and a commercial reactor.
 - The reduced heat removal capability in the commercial reactor caused by the smaller heat transfer area to reactor volume (A/V ratio).
2. Did the equipment used in the laboratory test adequately simulate commercial equipment? For example, chemical compound stability studies are often determined in a laboratory oven. If the material will be subject to high shear rates in the commercial equipment, laboratory oven studies may not be sufficient.

11.6 EXPLANATION TO OPERATING PERSONNEL

An explanation of the plant test should be given to operating personnel (and perhaps mechanical personnel). This explanation can be conducted in a training session, with a written handout or by one-on-one discussions. The following items should be included:

1. Purpose of the test—The value of the test for the overall company objectives should be explained to the operating and mechanical personnel. The plant test could be directed at solving an operating problem that will make for an easier job or producing a superior product that will lead to increased sales. Regardless of the goal of the test, this is an opportunity to build enthusiasm for the test by explaining that the success of the enterprise leads to both job security and promotional growth for the individual.
2. How was safety evaluated?—Unfortunately, most hourly personnel have had experiences with plant tests or plant changes where safety was not adequately considered. This explanation should consider new chemicals, new laboratory procedures, and new operating or mechanical conditions/procedures. Many operating companies have safety and peer review committees that review new operating changes. The operations and mechanical workers should be informed of the details of these reviews. In addition, if new chemicals are involved, the MSDS sheets should be reviewed with the appropriate personnel and posted in visible places.
3. Why the test will work—This will be an opportunity to explain to the hourly worker the theory behind the proposed test. Most theoretical explanations can be expressed in terms that even people without engineering degrees can understand. This is an important step and should not be considered just a requirement, but it should be looked on as an opportunity to educate and obtain “buy-in” for the test.

4. How will the test be evaluated?—The purpose of this explanation is twofold. It is an opportunity to explain exactly what will be considered in evaluating the test. It may be desirable as part of the test to have the hourly worker fill out data sheets. The accuracy of this will be a function of how well he understands how the values will be used. In addition, this will be a time to explain that a test that does not prove the hypothesis is not a failed test. The only failed tests are those that are not conclusive.
5. If the test works, what does he get from it—The hourly worker will often have questions such as:
 - If the test is successful and changes in operating or mechanical procedures are required, will it make my job easier or harder?
 - Will these changes reduce manning or limit future addition of jobs?
 - If the test is successful, how do I get any credit for doing all this extra work?

These are questions that are often not brought up. However, they are almost always in the minds of the hourly workers. Ignoring them will usually leave it to the operator or mechanic to assume the “worst case” answers.

11.7 FORMAL POST-TEST EVALUATION AND DOCUMENTATION

The formal post-test evaluation and documentation phase of the plant test is often one of the most overlooked areas of plant test execution. The desire to improve organization efficiency often creates pressures to move on to the next plant test to solve the current problem or to move on to the next problem to be solved. Whether the test proved or disproved the working hypothesis, the benefits of the documentation are to provide a lasting reference that will help avoid repeating the test or even worse avoid future changes that will cause the problem to reoccur. In addition, as indicated earlier, the writing process will often clarify the thinking process and improve problem-solving activity.

A plant test that disproves the hypothesis is often not documented because the problem solver does not see this as important. He feels the need to move on and work on the next hypothesis to get to a problem solution. The failure to document successful plant tests that disprove the hypothesis will often cause a similar hypothesis to be proposed at some future time. Thus, the failure to document the work, because of the alleged need to be efficient, will cause a loss in organization efficiency. A comment often made by many experienced operating and/or mechanical personnel when presented with a proposed plant test is “We tried that before and it didn’t work”. This is an indication that formal documentation of previous tests is not being done.

Even more serious is the failure to document a plant test that proved a working hypothesis. In this scenario, changes are made which eliminate the

problem. Several years later, a proposal is made to reverse the changes to try to solve another problem, increase production or improve product quality. When the question is raised “Why are we operating at these particular conditions”, no documentation exists to show the fact that changes were made to eliminate an operating problem. Thus, the assumption is made that the conditions can be returned to the previous conditions.

Another scenario is the case of a failed plant test. That is, one that neither proves nor disproves the working hypothesis. Rather than making another attempt with an improved plant test that will be successful (prove or disprove the hypothesis), the approach is just completely abandoned. No documentation is done to indicate why the test was not conclusive. At a later point in time, the hypothesis is reintroduced. When a similar test is proposed, the memories of both technical and operating personnel are “We tried it before and it didn’t work”. Actually, the validity of the hypothesis is unknown. What is known is that the test did not prove that the hypothesis was correct. The converse that the test proved that the hypothesis was incorrect is not true. Because the recollection is that the test did not work, the hypothesis is abandoned. A good documentation of the previous test would have indicated that what failed was the test itself rather than the hypothesis being incorrect.

The size of the actual document should be minimized. It should include items such as the objective of the test, the test procedure, the test results and the conclusions. In addition, any comments concerning safety should be included. Because of the technical conclusions and the possible need to incorporate changes into operating conditions or procedures, the final document should be approved by both operating and technical management.

11.8 EXAMPLES OF PLANT TESTS

Some plant tests to verify hypotheses will be simple and some will be more complicated. The next few pages present two examples of involved plant tests that were directed at improving a product and/or process. While they are not directly related to solving plant problems, they are real-world examples that illustrate the concepts discussed above. These same concepts are applicable to plant tests directly associated with solving plant operating problems.

11.9 EXAMPLE PLANT TEST 11-1

A synthetic rubber producer was pressured by customers to change stabilizers to one that would continue providing a product that did not discolor due to stabilizer oxidation, but would have better product-related properties. Based on the customer request, a new stabilizer was identified by the technology organization. Tests to confirm the stabilizing and non-discoloring properties were conducted at different temperatures in ovens. These tests were conducted by first mixing the stabilizer with the polymer at ambient temperatures

in low-intensity mixers. The polymer containing the stabilizer was then heated and held at elevated temperatures in the oven. These tests confirmed that the product did not discolor and that the molecular weight of the polymer did not change even after several hours in an oven. Thus, the new stabilizer seemed to meet the goals. That is, the product did not discolor and the molecular weight did not decrease, indicating that the new additive was an effective stabilizer.

The actual synthetic rubber process consisted of a polymerization section where the stabilizer was added to a slurry of rubber and water. This slurry was then pumped to the finishing section where the rubber was dried to remove water, extruded and rolled on hot mills to put the final product into a form that could be boxed and shipped to the customer.

A plant test was scheduled to assess the utilization of this new stabilizer in the plant. The hypothesis being tested was that the new stabilizer could be added effectively in the plant and that it would be as efficient as indicated in the laboratory results. Since the laboratory data indicated that the stabilizer was very effective, only some of the steps listed earlier were implemented. These steps and what was actually done are summarized below:

1. **Pretest Instrument and Laboratory Procedure Evaluation**—For the most part, this was done in a satisfactory manner. The laboratory was well prepared to analyze for the stabilizer and in addition, instruments were adjusted for the slightly different density.
2. **Statement of Anticipated Results**—Since the technology experiments indicated that such good results were obtained, very little was done to prepare a statement of anticipated results. It was just assumed that the stabilization properties would be comparable to the existing stabilizer or even better. That is, there would be no change in molecular weight during the finishing operation.
3. **Potential Problem Analysis**—Actually very little was done to develop a potential problem analysis. The technology work was so convincing that this new stabilizer would meet the criteria of not discoloring and avoiding molecular weight change in the finishing operation that this phase was just ignored. It was anticipated to be a “boring test”.
4. **Explanation to Operating Personnel**—This was not done.
5. **Formal Post-test Evaluation and Documentation**—As discussed later, the test disproved the hypothesis so conclusively that it was mandatory to document the results of the test.

Since based on technology testing, it appeared that the new stabilizer had stabilizing properties equivalent to the current stabilizer, all operating conditions such as polymer molecular weight and amount of stabilizer added were held constant and operations were simply switched over to the new material. Very soon, the molecular weight of the product leaving the finishing operations began to decrease rapidly even though the molecular weight in the

polymerization operations did not change. This was completely the opposite of what would be expected if the stabilizer was performing as anticipated based on the technology tests. The lack of a well thought-out potential problem analysis before the test was now causing a panic problem-solving attempt during the test. The two different groups involved (operations and technical) began pursuing different approaches.

The operating group increased the molecular weight in the polymerization section in an attempt to make “on-specification” product leaving the finishing section. Since the molecular weight in the polymerization process was inversely proportional to the monomer conversion, it was necessary to reduce the monomer conversion in order to increase the molecular weight. This lowered monomer conversion tended to overload the monomer recycle system. The operations continued to deteriorate. The molecular weight in the finished product continued to fall and the monomer conversion continued to be decreased as a compensatory action. The test was aborted after only a few hours of operation.

The technical/technology group initiated problem-solving activities. An analysis of the final product indicated that there was very little stabilizer present. This brought up several potential hypotheses:

- An incorrect amount of stabilizer was being added.
- The stabilizer was being washed off the polymer in the water slurry operation.
- The stabilizer was being vaporized in the finishing operation even though long-term technology tests in the ovens indicated this would not occur.
- The laboratory results were wrong and stabilizer really was present at the desired concentration.
- There was the target amount of stabilizer in the polymer; it was just not an effective stabilizer. This would be in conflict with the technology data.

An evaluation of the data after the test was aborted, indicated that the stabilizer was being added at a correct rate and was not being washed off the polymer in the water slurry operation. However, it was being vaporized in the high-shear zone of the extruder and hot mills. These zones were not only at elevated temperatures, but the high shear caused large amounts of the surface to be exposed to the atmosphere. This was a radically different condition than experienced in the low-shear environment of the ovens.

11.10 LESSONS LEARNED

There are several lessons that can be learned from this plant test. They involve several areas such as the failure to conduct a potential problem analysis, the

failure to provide an explanation to operating personnel, the blind acceptance of technology data without questioning the basis for conclusions and the attitude that this is going to be a “boring plant test”.

A potential problem analysis would have very likely uncovered that the shear rates in the extruder/mills were vastly different than those in the very low shear drying ovens. This consideration would have generated additional technology work to try to simulate the high shear rate. This additional work would have likely shown that large amounts of stabilizer were lost in the high shear rate studies. If the proposed stabilizer still appeared to be the best available, the plant test could have been conducted at much higher stabilizer addition rates to compensate for the vaporization of the stabilizer in the extruders and mills. A potential problem analysis would have also led to consideration of the overloading of the monomer recycle system that occurred when the conversion had to be dropped to a low level to obtain the specification molecular weight in the finished product. Plant tests where technology data are accepted blindly and/or where the test is considered to be boring will almost always result in failure of some kind.

The lack of a careful and detailed explanation of the plant test to the operating personnel did not impact the results of this first test. However, when another test was scheduled, there was a considerable amount of tension caused by the failure to adequately explain the goals and purposes of the first test.

11.11 EXAMPLE PLANT TEST 11-2

As a second illustration of a plant test, consider the following example. It was desirable to test the capacity of a single reactor in a plant that used two reactors in series. This would allow assessing the possible low cost debottlenecking of the existing plant as opposed to the alternative of building a new plant. If the single reactor could be operated at the same capacity as the existing two reactors in series, it would be possible to increase the existing plant capacity by at least 50 percent. The hypothesis to be tested was that a single reactor could produce at the same production rate as two reactors in series with no increase in fouling rate.

The reactor was a boiling reactor where the heat of reaction was removed by the vaporization of the reactant which was then condensed and returned to the reactor. The reaction product consisted of small insoluble solid particles. Because of the size of the particles, some of them were always entrained with the vapors leaving the reactor. The vertical condenser used to condense the reactant was provided with trays to allow washing the entrained solids back into the reactor. A sketch of this system is shown in Figure 11-1.

A plant test was deemed necessary since at the higher vapor rates associated with the higher reactor capacity, more entrainment might be encountered. The increased entrainment might lead to fouling of the exchanger, the vapor line, or the liquid return line. In addition, the liquid handling capacity

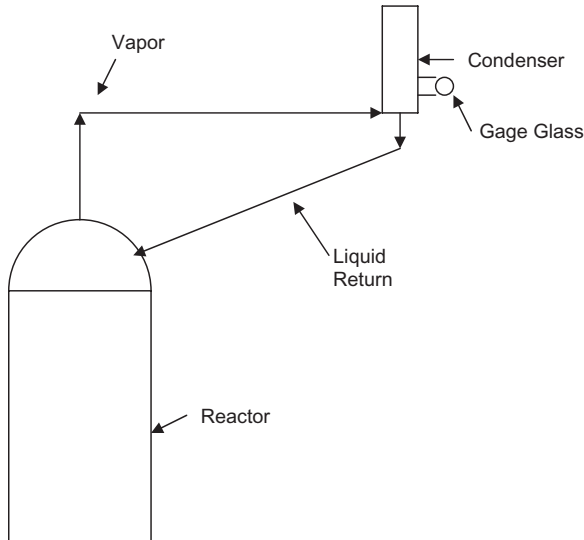


Figure 11-1 Reactor/overhead condenser schematic.

of the return line under possible fouling conditions was uncertain. It was necessary to develop techniques for monitoring the possible fouling of the exchanger, as well as the vapor line and liquid return line.

Three techniques were developed to monitor operations and fouling during the test of the single reactor. They were as follows:

1. The heat transfer coefficient on the overhead condenser was monitored hourly by the process control computer.
2. A local level gauge on the bottom of the exchanger was monitored every 2 hours by visual observations. An increase in the liquid level in the bottom of the exchanger would indicate that the condensate was not flowing back into the reactor freely. That would mean that the liquid return line was likely partially plugged.
3. The vapor and liquid lines to and from the exchanger were “rung” every 2 hours. This “ringing” was a process of lightly tapping on the line with a hammer. If fouling was beginning to occur in the line, the pitch of the ring would have changed from a sharp clear ring to a dull thud. While this qualitative test was not described in textbooks, it had been proven by operating personnel in earlier experiences.

The manual monitoring (local level gauge and “ringing the lines”) required the operating personnel to climb six flights of stairs in order to reach the desired physical area of the equipment.

As indicated earlier, there are five things that are essential to a successful plant test. For this plant test, these items were covered as follows:

1. **Pretest Instrument and Laboratory Procedure Evaluation**—This was relatively simple for this test. The calibration of instrumentation that would allow determining the exchanger heat transfer coefficient was part of a routine task order. However, as indicated later, it was necessary to re-range several instruments to allow operation of the reactor at higher capacity. The manual procedures for checking the level and condition of the vapor and liquid lines were well established by previous experiences with solids entrainment.
2. **Statement of Anticipated Results**—Prior to the plant test, the heat transfer coefficient on the condenser was determined from the existing temperatures and heat duty. Calculations were made to determine what the anticipated inlet and outlet water temperatures would be at the anticipated heat duty. These calculations assumed that the heat transfer coefficient would be slightly lower than that determined at the existing duty. This was done to allow for a higher thickness of condensate flowing down the tubes. The actual change in condensate thickness would be very difficult to calculate with any accuracy. Thus, the reduction in overall heat transfer coefficient caused by the thicker condensate layer was assumed to 10 percent. Calculations were also made to confirm that the vapor and liquid lines had adequate capacity in their clean conditions. Operations personnel had a good intuitive feel for what a clean line sounded like when it was “rung”. Thus, an overall statement of anticipated results would indicate the following evaluation of the reactor overhead circuit was expected:
 - Based on the anticipated heat transfer coefficient, the anticipated values of the water temperatures and flow rates around the condenser were estimated. These were included in the anticipated results.
 - Based on calculations, there was anticipated to be no level in the bottom of the exchanger. In this case, the calculations indicated that the liquid and vapor lines in a clean condition had sufficient capacity so that there should be no level buildup in the exchanger.
 - The overall statement included a comment that the vapor and liquid return lines should “ring” with a clear sound.

As with any process equipment or operating condition changes, safety must be considered. At the higher reaction rates, the safety valves would be required to release at a higher rate in an emergency. The required and actual capacities of the valves were reviewed and it was found that the capacity of the valves was greater than the maximum anticipated release rate. After other potential safety problems had been evaluated, a statement was provided indicating that no safety problems were anticipated.

Other areas of the process were also considered to evaluate the effect of operating at full rates with only a single reactor. An evaluation of the catalyst feed system to insure that adequate catalyst supply would be

available was conducted. The catalyst efficiency was anticipated to decrease as reactor volume was removed from service. All of the instrumentation for the reactor to be operated at the higher rate was evaluated and meter ranges increased where necessary.

3. **Potential Problem Analysis**—In the case of this plant test, there were potential problems associated with the overhead condenser, as well as at other locations in the plant. Trigger points were developed for the heat transfer coefficient on the overhead condenser. This variable was routinely calculated by the process control computer and a trigger point was set to insure that the reactor temperature did not “run away”. A reactor temperature “run away” could occur if the heat transfer coefficient on the condenser is so low that a slight increase in reaction rate would cause the heat generated to increase at a faster rate than heat removal capabilities. This was explained in detail in Chapters 4 and 9. The trigger points for the liquid level in the condenser and for the “ringing” of the lines were more qualitative. Any accumulation of liquid in the condenser or “line ringing” that was not clear was set as a trigger point.

Often when focusing on certain areas of the plant for a plant test, other areas are overlooked. As indicated above, the catalyst feed rate was anticipated to increase due to the reduced residence time associated with using a single reactor. Since the reactor was a boiling reactor, some of the reactor volume below the liquid level was bubbling vapor. As such it would not be effective reaction volume. Correlations were used to estimate the effect of the higher “boil up” rate associated with the increase in production on the bubbling vapor volume of the reactor. As the “boil up” rate increased the correlations predicted that the bubbling vapor volume below the liquid level increased and the effective reaction volume decreased. The potential problem that these correlations were inaccurate was considered. If the reduction in reactor volume, associated with the bubbling vapor, were greater than expected, the catalyst efficiency would be lower than anticipated. Thus, a trigger point was included for catalyst efficiency. Other trigger points were determined for other parts of the process where potential problems were anticipated. The key thing to consider is that having the well thought-out potential problem analysis allows for reacting to situations in a predetermined way rather than in a reactionary mode in the “heat of battle”.

4. **Explanation to Operating Personnel**—Most operating and mechanical personnel were happy to hear that their efforts to make a good product resulted in consideration of an increase in capacity. However, they had concerns that had to be addressed in order to obtain their cooperation for the plant test. Some of these comments and concerns were:
 - “We don’t have time to climb stairs and do the checks every 2 hours.”
 - “You guys will get all the credit while we do all the work.”

- “Won’t running the plant at a higher rate make more work for me?”
- “If we expand by adding more plants that will mean more jobs for my friends and family. This “debottlenecking” expansion doesn’t add any jobs.”
- “Is it really safe to operate the reactor in this fashion?”
- “I don’t see how we can run this reactor at higher rates when we are having problems with carryover at the lower rates.”

Essentially all of the questions that might come from the operating or mechanical personnel are in two categories. There are questions that can be answered based on calculations that have already been done as part of the pretest efforts or potential problem analysis. The value of doing the calculations is that the operator can be told, we have considered that and it is ok. The question of reactor safety is an example of this. It is always possible that a question will be raised which has not been considered. *Serious consideration* should be given to any question of this nature.

There will also be questions that cannot be answered based on calculations. Many of these will require an explanation that deals with company goals or the competitive situation. For example, the desire to expand by building more small plants could be answered by the fact that competitors are building larger plants and that being competitive with them provides job security. This job security for the employee is more important than creating jobs for friends and family.

5. **Formal Post-test Evaluation and Documentation**—While the test appeared to confirm the hypothesis, a formal test document was still prepared. The formal test evaluation and documentation included the conclusion that the heat transfer coefficient of the condenser at the higher rates was comparable to that at the normal rates. The slightly higher condensate thickness did not cause any decrease in heat transfer coefficient. When the heat transfer coefficient was evaluated as a function of time, there was no indication that fouling was occurring during the test. In addition, there was no indication of fouling as gauged by the absence of any level in the condenser and the clear sound of the “pipe ringing” during the test.

The catalyst efficiency anticipated at the higher rates was compared to the actual catalyst efficiency. Since these values were very close, it was concluded that no unanticipated loss in reactor volume associated with vapor bubbling occurred during the test.

Perhaps one thing that is often overlooked in documenting a plant test is the comments from mechanics or operating personnel. Comments of operating personnel were included. Their comments were that things ran very smoothly during the test.

11.12 LESSONS LEARNED

This test was very successful from the standpoint that the results indicated very conclusively that it would be possible to operate the reactors at significantly higher rates. Even if the conclusions had been that it would not be possible to operate the reactors at high rates, the test would have been successful. The results would have been conclusive. As indicated earlier, a successful plant test is one where the test result is conclusive.

Several lessons were learned from this test. While the time to do the pretest calculations and potential problem analysis may seem to be inefficient, it provided a basis to convince management and operations personnel of the feasibility of the test. It also provided a basis for determining trigger points to allow a predetermined decision on aborting the test.

Using any short-term test to make decisions about fouling is difficult. The risk of concluding that fouling was not occurring was ameliorated by obtaining the maximum amount of data. In this case, three different techniques were used to monitor fouling.

There are always potential problems associated with any plant test. In the earlier example (Test 11-1), the anticipation that the test was going to be boring was radically different than the anticipation for this test.

Even in tests that appear to confirm a hypothesis, documentation of the results is important. In this test, it was obvious that the results associated with fouling should be documented. In addition, the analysis of the expected catalyst efficiency at the higher rates and the higher “boil up rate” proved very valuable. Without this analysis and documentation, erroneous conclusions regarding the reduced catalyst efficiency encountered as rates were increased might have been reached.

11.13 MORE COMPLICATED PLANT TESTS

Frequently, it will be necessary to consider conducting a plant test where the cost of a plant shutdown is so great that “in-depth” theoretical *comparative* studies must be done as part of the potential problem analysis. These studies will allow determining the risk of such an event by a comparison to existing operations. These comparative studies will not provide absolute values, but will allow determination of whether the plant test will increase or decrease the item of concern. An example of this might be a gas-phase reaction process where the presence of fines (small particles) could cause entrainment with a subsequent plant shutdown. Fines are known to be present with the current catalyst. However, the exact concentration is not known. The level of fines associated with the current catalyst results in minimal shutdowns. There are theoretical techniques available to predict the amount of fines produced by the catalyst knowing the catalyst attributes (reactivity, particle size and particle size distribution) and reaction conditions.

A plant test using a new catalyst with radically different attributes in the gas-phase reactor was proposed. Concerns were expressed about the potential for this test causing a plant shutdown. In this case, the *absolute* level of fines was not as important as answering the question—“Will the amount of fines increase or decrease?” In order to assess the risk of a plant shutdown if a plant test is run with the new catalyst, calculations were done to estimate the amount of fines produced by both the existing and new catalysts. These calculations were then compared and an assessment made regarding the possibility of increased fines. If this assessment indicated that there will be a comparable or lower level of fines produced, then there is a high probability that the plant test can be conducted without shutting down the plant. Conversely if the calculations indicate that the fines level will increase, a plant shutdown is a definite concern. In this case, it might be better to redesign the catalyst rather than risk a plant shutdown caused by the test of a new catalyst.

11.14 KEY PLANT TESTS CONSIDERATIONS

The key thing to remember from this chapter is that if a plant test is used to confirm the hypothesis, it must be well planned with an aim to thoroughly prove or disprove the hypothesis. Successful plant tests are those that either confirm or reject the proposed hypothesis. Documentation of the plant test results regardless of the conclusion is imperative.

UTILIZATION OF MANUAL COMPUTATION TECHNIQUES

12.1 INTRODUCTION

The modern day widespread availability of desktop and laptop computers, along with process engineering programs, allows the chemical engineer to quickly simulate fractionation or flash calculations. In addition, the widespread availability of component databases and equations of state/equilibrium algorithms enhances the ability of the computers to do such calculations. Because of the expansion of the technology, it may seem that manual calculations are now obsolete. However, there is still a place for manual calculations. While the computer simulation programs are very precise, they also depend on accurate input data and good convergence routines. In addition, they are generally best suited for design rather than problem solving.

The use of any computer program also creates the risk of “user ignorance”. That is, the user of the program simply will provide input data without understanding the algorithms used to perform the simulation. In using process engineering simulations, the program user must have a good understanding of the computer program to be used. This understanding has to be more than an understanding of how to “fill in the blanks”. The user must understand how the algorithm works. Understanding of how to do the manual calculations will help provide the ability to comprehend the simulation programs.

The manual calculations discussed in this chapter include both of the following:

- Calculation techniques which were once well known and taught in the academic world, but have been forgotten due to lack of use.
- New techniques with which the problem solver may not be familiar.

The problems at the end of the chapter are given to illustrate these calculation techniques and are not in the format used in this book, for example, problems illustrating the five-step problem-solving approach.

Manual calculations are often of value as a “ballpark” check on the computer simulation. Using the techniques discussed in this chapter will provide means to perform checks on computer simulations. While manual calculations can never be as accurate as computer simulations, they provide a potential method to confirm that computer simulations are reasonably accurate. While the computer will not make calculation mistakes, it is subject to three sources of error as follows:

1. Programming errors. The simulation programmer may have made either a blatant or subtle error in the simulation. The blatant errors are almost always discovered and corrected prior to widespread use of the program. The subtle errors are often not detected until after months or years of use. An example of a subtle error is the simulation that uses numerical integration with a limited number of numerical increments. The simulation may work for years and give exact answers. However, it then fails to give the correct answer for a very specialized case that requires a greater number of increments than used in the simulation. While this subtle error may be easily modified, the design and construction of the facilities based on the erroneous simulation may have already been completed.
2. The user of the simulation may have made a mistake in the input data. While this can also occur when doing manual calculations, the act of doing manual calculations will often allow discovering simple input errors.
3. In his hurry to complete a computer simulation, the problem solver may compromise the validity of the solution by selecting inappropriate vapor–liquid equilibrium techniques, simulating a component not available in a database with an inappropriate substitute, or accepting a less than acceptable convergence.

Unfortunately, once a computer simulation has been finished and presented, it has a great deal of credibility whether it is correct or not.

Manual calculations for binary systems can often be done quicker than computer simulations. This is especially true for the problem solver that often finds himself in a process plant control center without full computer simulation capabilities. This situation might also occur if the problem solver is in a country other than his own where he does not have access to a computer either

due to security or language limitations. In these situations and others where the process problem solver has available to him vapor pressure curves for the components under consideration, very good simulations of binary systems can be made by manual calculations. This area is discussed below in Sections 12.2 through 12.7.

Manual calculations can often provide good approximations of complicated equilibrium systems such as those involving a polymer and a solvent. Many times the equilibrium between a polymer and a solvent is simulated by assuming that the polymer acts as the heaviest hydrocarbon available in the component database. This assumption may well be valid for high concentrations of solvent in the polymer. However at the low concentrations (almost always important when dealing with a solvent dissolved in a polymer), this is rarely true. This area is discussed in Section 12.8.

12.2 BINARY SYSTEMS

As indicated earlier, manual calculations for a binary system can be very accurate if vapor pressure curves or equilibrium constants are available for the components under consideration. Some areas where manual computation techniques can be done quickly and are of great value in binary systems are as follows:

- Estimating quickly the vapor and liquid compositions of a binary mixture.
- Estimating quickly the equilibrium of water that is dissolved in a hydrocarbon.
- Estimating quickly the vapor phase concentration when two liquid phases are present.
- Estimating quickly the condensation temperature of a gaseous mixture that contains both water and hydrocarbons.

The following paragraphs present examples of each area.

12.3 ESTIMATING THE VAPOR–LIQUID COMPOSITIONS OF A TWO-PHASE BINARY MIXTURE

The phase rule given earlier and reproduced below can be used to understand how the composition of each phase of a binary system can be determined.

$$F = C - P + 2 \quad (10-1)$$

Where:

F = the degrees of freedom (temperature, pressure and composition)

C = the number of components in the mixture

P = the number of phases present

Thus for a binary ($C = 2$) vapor-liquid mixture ($P = 2$), fixing the temperature and pressure reduces the degrees of freedom to 0. Thus, both liquid and vapor phase compositions are fixed.

For example, if a two-phase mixture of propane and isopentane exists at 150°F and 18 atmospheres, the composition of each phase can be calculated as follows:

Step 1

Determine the equilibrium constant for each component. These can be determined either from charts of equilibrium constants as a function of temperature and pressure or by using the relationship shown below:

$$K = VP/\Pi \quad (12-1)$$

Where:

K = the equilibrium concentration of the desired component

VP = the vapor pressure of the component at 150°F

Π = the total pressure

Step 2

Assign the following values:

X = the composition of C_3 in the liquid phase, mol fraction

$1 - X$ = the composition of $I-C_5$ in the liquid phase, mol fraction

Y = the composition of C_3 in the vapor phase, mol fraction

$1 - Y$ = the composition of $I-C_5$ in the vapor phase, mol fraction

Step 3

Solve for X , $1 - X$, Y and $1 - Y$ using equations (12-2) through (12-5) and the calculation format shown in Table 12-1A. The results are shown in Table 12-1B.

$$Y_i = K * X_i \quad (12-2)$$

$$\sum Y_i = 1.0 \quad (12-3)$$

Table 12-1A Calculation format

Component	Liquid, mf	K	Vapor, mf
C ₃	X	1.28	1.28 * X
I-C ₅	1 - X	0.171	0.171 * (1 - X)
Total	1.0		1.0

Table 12-1B Results of calculations

Component	Liquid, mf	Vapor, mf
C ₃	0.748	0.957
I-C ₅	0.252	0.043

$$1.28X - 0.171X = 1 - 0.171 \qquad (12-4)$$

$$X = 0.748 \qquad (12-5)$$

12.4 ESTIMATING THE EQUILIBRIUM CONSTANT OF WATER THAT IS DISSOLVED IN A HYDROCARBON

Estimating the volatility of water relative to the hydrocarbon in which it is dissolved, is often required in process engineering calculations. The volatility is the ratio of the equilibrium constant of water to the equilibrium constant of the hydrocarbon. While it may seem apparent that water with a boiling point of 212°F is less volatile than lower molecular weight hydrocarbons such as propane and butane, this is not true if the water is dissolved in the hydrocarbon. Water is a very unique molecule. Based on the atomic structure and molecular weight, it should be a gas under atmospheric conditions. The reason that water (molecular weight = 18) exists as a liquid rather than a gas is due to hydrogen bonding between the water molecules. This hydrogen bonding causes water to behave like a much higher molecular weight material and boil at the higher temperature. When water and hydrocarbons exist together, the water can either exist dissolved in the hydrocarbon or as a separate phase. The volatility of water associated with a hydrocarbon depends on whether the water is dissolved in the hydrocarbon or exists as a separate phase.

The volatility of water that is completely dissolved in hydrocarbon is greatly enhanced due to the breakdown of the hydrogen bonding. This breakdown results in water being more volatile than even low molecular weight hydrocarbons (propane for example). The enhanced volatility of water created by the breakdown of hydrogen bonding allows water to be removed from hydrocarbons in some processes by taking water as an overhead product. Such a drying by fractionation process is shown in Figure 12-1.

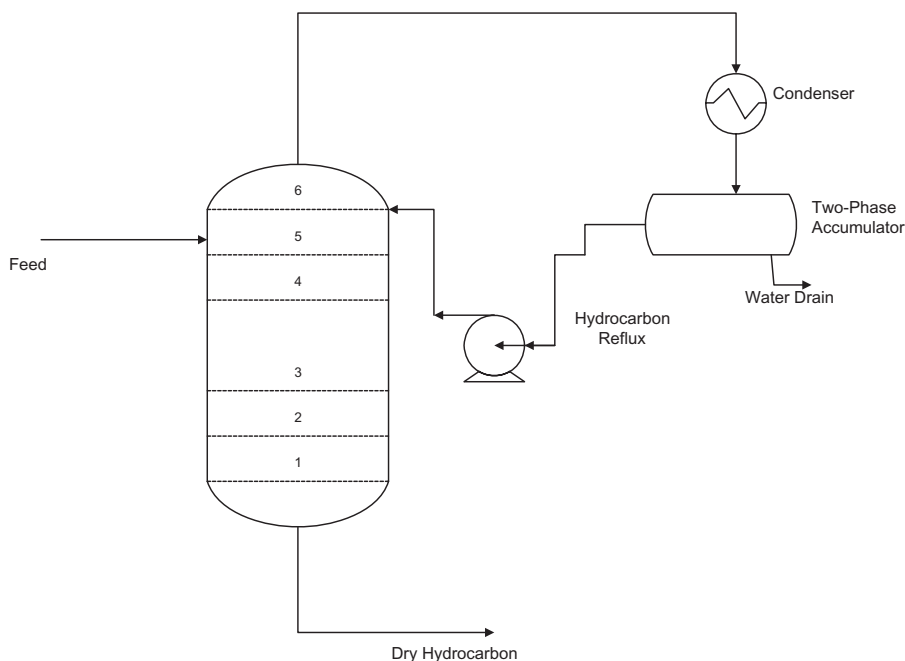


Figure 12-1 Drying by fractionation.

Often it is desirable to estimate the equilibrium constant and hence volatility for water dissolved in a hydrocarbon to allow designing a distillation column such as shown in Figure 12-1. Some simulation programs can correctly handle water that exists as a second phase or dissolved in the hydrocarbon.

The volatility of water can also be estimated by manual calculations. This can be done by remembering that *the activity of a component in all phases is equal* and assuming that the hydrocarbon is essentially saturated with water.

This can be expressed mathematically as follows:

$$A_w = A_v \quad (12-6)$$

$$VP = PP = Y * \Pi \quad (12-7)$$

$$Y = K * X \quad (12-8)$$

By substitution:

$$K = VP/(X * \Pi) \quad (12-9)$$

Where:

A_w = activity of water in the hydrocarbon phase if it is dissolved in the hydrocarbon

- A_v = activity of water in the vapor phase
 K = the equilibrium constant of water dissolved in any hydrocarbon
 VP = the vapor pressure of pure water at the chosen temperature
 Π = the total pressure which will be approximately the vapor pressure of the hydrocarbon
 PP = the partial pressure of water vapor
 Y = the concentration of water in the vapor phase, mol fraction
 X = the saturation concentration of water in hydrocarbon at the chosen temperature, mol fraction

Equation (12-9) indicates that the equilibrium constant for water in any hydrocarbon at saturation can be estimated knowing only the saturation concentration and the vapor pressure of water and the hydrocarbon. This approach is based on the following assumptions:

- Since the water concentration in the hydrocarbon phase is assumed to be at saturation (that is, a single additional drop will cause formation of a separate water phase), the vapor pressure of water can be assumed to be that of pure water. The vapor pressure should be very close to the activity. These assumptions allow the translation of the left-hand side (LHS) of equation (12-6) to the LHS of equation (12-7).
- As equation (12-7) shows, the activity is assumed to be equal to the partial pressure or the vapor phase concentration multiplied by the total pressure.

While the expert in thermodynamics may consider the approach described above less than desirable, it is more than acceptable for plant problem solving.

As indicated above, this approach is applicable for estimating the equilibrium constant for water dissolved in a hydrocarbon when the hydrocarbon is saturated with water. If the concentration is below the saturation level, the equilibrium constant for water will likely be even higher. This is expected because as the concentration of a component in a nonideal system decreases, the deviation from ideal increases.

12.5 ESTIMATING THE VAPOR PHASE CONCENTRATION WHEN TWO LIQUID PHASES ARE PRESENT

Two immiscible liquid phases are often present with hydrocarbon and water mixtures. It is often desirable to estimate the vapor phase composition in equilibrium with the two liquid phases. An example of this might be a knock-out drum that contains both water and a hydrocarbon. If the vapor phase from

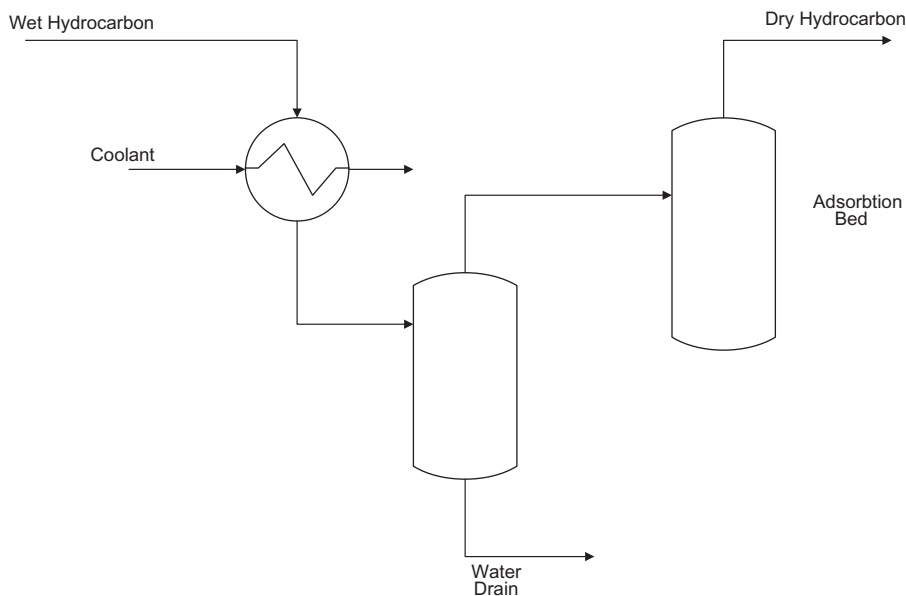


Figure 12-2 Drying with condensation and adsorption.

the drum is to be dried in an adsorption bed, it will be necessary to know the water content of the vapor leaving the knockout drum. Such a process is shown in Figure 12-2.

The vapor phase composition can be estimated by the simple rule that each liquid phase exerts its own vapor pressure.

Thus:

$$\Pi = VP_W + VP_{HC} \quad (12-10)$$

Where:

Π = the total pressure of the two liquid phases

VP_W = the vapor pressure of the water phase

VP_{HC} = the vapor pressure of the hydrocarbon phase

For any given system if the total pressure (Π) and vapor pressures of the hydrocarbon and water are known, then the vapor phase composition in mol fraction can be calculated as follows:

$$Y_W = VP_W / \Pi \quad (12-11)$$

$$Y_{HC} = VP_{HC} / \Pi \quad (12-12)$$

Where:

Y_w = the mol fraction water in the vapor phase

Y_{HC} = the mol fraction hydrocarbon in the vapor phase

12.6 CONDENSATION INTO TWO LIQUID PHASES

A converse of Section 12.5 is the case where a vapor phase containing both a hydrocarbon and water is condensed. In this situation, the temperature of the vapor is reduced until condensation of the vapor begins. Both the initial condensation temperature and which phase (water or hydrocarbon) condenses first depend on the initial composition of the vapor phase. Determination which phase will condense first, the initial condensation temperature, and the subsequent temperature at which formation of a second liquid phase occurs can be determined by the single process engineering concept as follows.

The partial pressure of a component in the vapor phase can never exceed the vapor pressure of the component at the given temperature.

Thus, one of the components (water or hydrocarbon) will begin to condense at a temperature of T_1 when the partial pressure exceeds the vapor pressure. This can be expressed mathematically as follows:

$$\Pi * Y_i \leq VP_i \quad (12-13)$$

Where:

Y_i = the vapor phase composition of the first component to condense

VP_i = the vapor pressure of the first component to condense

The initial component will continue to condense by itself until the temperature of the vapor is reduced to the point (T_2) where the sum of the vapor pressures is equal to the system pressure. At this point, equation (12-10) is satisfied and condensation of the second component will begin. The temperature (T_2) will stay constant until the entire second component is condensed. At this point, there will be no vapor left to condense. Additional heat removal will serve to cool the liquid. The vapor phase composition of component "i" (the first component to condense) between T_1 and T_2 can be estimated knowing the temperature as follows:

$$Y_i = VP_i / \Pi \quad (12-14)$$

It should be noted that the concept described above that:

The partial pressure of a component in the vapor phase can never exceed the vapor pressure of the component at the given temperature.

can also be used to evaluate the validity of plant laboratory or instrument data. For example, vapor phase analytical data must satisfy equation (12-13). The term $\Pi * Y_i$ cannot exceed VP_i . If it does exceed VP_i , it is highly likely that composition is wrong.

12.7 SHORTCUT FRACTIONATION CALCULATIONS

Computer fractionation simulation programs can be used to both design new distillation towers and to “problem solve” existing towers. Most of the simulation programs are intended for design calculations. They can be used for problem solving, but to operate in this mode often requires iterative procedures. For example, the design of a distillation column requires an input of feed and product compositions, rates, tray efficiency and a criterion for setting the reflux ratio. The reflux ratio is generally set at a multiple of the minimum reflux ratio, which is calculated by the computer simulation program. The simulation program can then size the tower. If problem solving is being done on the same tower, the reflux ratio and the number of actual trays are fixed. The tray efficiency must be adjusted to obtain a match between calculated and actual product compositions.

Even though the computer simulation programs are used for the fractionation calculations, there are some advantages to knowing shortcut fractionation techniques. Knowing these techniques will aid in understanding the results of the simulation, as well as being able to check the simulation results. Being familiar with shortcut calculation techniques will also be of value on occasions when a quick answer is required to an immediate problem. As indicated earlier, the computer will not make computational errors; however, it will only do what it is told to do. There are three types of errors that might occur in any simulation. These were described in Section 12.1.

Shortcut fractionation calculations can be used to confirm that computer simulations are giving “directionally correct” answers. In addition, these shortcut calculations can often be used to analyze poor performance in an operating tower in a more expeditious fashion than is possible with a full computer simulation program. These shortcut calculations can be “set up” on a spreadsheet with a minimal amount of effort. This is as opposed to computer simulations which are quick to run, but take time to “set up” and develop input data in the correct format.

One of the most valuable parts of a computer simulation program is the capability to determine the minimum reflux ratio for a multicomponent system. Since in a plant operating column, the reflux ratio is already known, determining the minimum reflux ratio may not be required. Prior to launching a rigorous simulation of an existing fractionation column, a shortcut calculation procedure should be considered. The possible reasons for considering a manual shortcut calculation approach are as follows:

Table 12-2 Shortcut calculations to simulate rectification section

Given:

- Number of theoretical rectification trays = 15
- Relative volatility (light key to heavy key) = 1.2
- Internal liquid to vapor ratio, mols/mol = 0.9
- Liquid concentration of light key on lowest tray, mol percent = 70
- Assumed concentration of light key in distillate, mol percent = 93

Note that if the calculated composition does not equal the assumed composition, a new assumption must be made and the calculations repeated.

- The shortcut calculation approach is much less complicated.
- The reflux ratio in an existing column is already known and the minimum reflux ratio generally does not need to be determined.
- A plant tower is often a binary fractionation or can be simulated as one.
- A plant problem often involves only part of the tower (rectification or stripping sections). Thus, a complete simulation is not required.
- For ideal systems (such as systems involving only hydrocarbon), a heat balance around each tray is not required since “equal molal overflow” is a good assumption. The assumption of “equal molal overflow” means that the internal liquid and vapor rates expressed in mols/hr will be equal throughout the tower if there is no addition or withdrawal of material or heat.
- The simplified vapor–liquid equilibrium constants that are used for the shortcut calculations are often much easier to develop than the more complex ones often required for the computer simulations.

Even if a rigorous simulation program is used to predict plant performance or to design a new tower, it will be of value to perform a shortcut calculation to confirm the validity of the simulation. As an example of a shortcut calculation, the rectification section of a tower is shown in Table 12-2. The calculation bases are given in steps 1 and 2 (equations (12-15) and (12-16)). This shortcut procedure assumes that the vapor-liquid equilibrium is constant in the tower and that equal molal overflow is a good assumption. A spreadsheet was developed and the results are shown in Table 12-3.

Calculation Bases

1. Equilibrium relationship between vapor and liquid on any tray

$$Y_N = \alpha * X_N / (1 + (\alpha - 1) * X_N) \quad (12-15)$$

2. Material balance relationship between vapor and liquid and overhead distillate product.

Table 12-3 Results of shortcut calculation

Tray Number	Compositions of Light Key in Mol Fraction	
	Liquid on Tray	Vapor Leaving Tray
15 (starting tray)	0.7	0.737
14	0.715	0.751
13	0.731	0.765
12	0.747	0.78
11	0.763	0.795
10	0.78	0.809
9	0.796	0.824
8	0.812	0.839
7	0.828	0.853
6	0.844	0.867
5	0.86	0.88
4	0.875	0.893
3	0.889	0.906
2	0.903	0.918
1 (top tray)	0.917	0.93

$$X_{N-1} = Y_N/R - X_D * ((1/R) - 1) \quad (12-16)$$

Where:

Y_N = vapor phase composition of light key on tray N, mol fraction

X_N = liquid phase composition of light key on tray N, mol fraction

X_{N-1} = liquid phase composition of light key on tray above tray N, mol fraction

α = relative volatility, light key to heavy key

R = internal liquid to vapor mol flow rate ratio

Light key refers to the component that is the most volatile.

Heavy key refers to the component that is the least volatile.

Table 12-3 summarizes the results of the spreadsheet calculations.

Since the vapor leaving tray 1 is condensed and is the distillate, the calculated composition equals the assumed composition.

These calculations can be simplified even further for a binary tower at constant temperature *where small quantities of a heavy key (lower volatility material) are being fractionated to low levels in the overhead product. In this case it can be shown that:*

$$X_{n+1} = (X_n * V * k)/L \quad (12-17)$$

Where:

- X_{n+1} and X_n = tray compositions of the *heavy key* in mol fraction, where tray $n + 1$ is above tray n
 V = the internal vapor rate in mols/hr
 L = the internal liquid rate in mols/hr
 k = the volatility of the *heavy key* relative to the *light key*. Note this will always be less than 1.

Equation (12-17) can be transformed into the equation below which can be used to make a quick estimate of the low-volatility material in the distillate product.

$$X_D = X_T * (V * k / L)^N \quad (12-18)$$

Where:

- X_D = composition of the heavy key in mol fraction in the overhead distillate product
 X_T = composition of the heavy key in mol fraction at the start of the rectification section
 N = number of theoretical trays in the rectification section

12.8 POLYMER-SOLVENT EQUILIBRIUM

The problem solver will often not have available to him simulations that allow predictions of polymer-solvent equilibrium. Faced with this dilemma, he often will select the heaviest component in the computer database for simulating a polymer. This may be adequate for solvent-polymer systems that contain solvent concentrations greater than 10 to 20 volume percent. However, below this level, the polymer begins to act to reduce the volatility of the solvent and the partial pressure of the solvent will be less than anticipated when the polymer is simulated using the heaviest component in the database. The converse will also be true. That is, at solvent concentrations below 10 to 20 volume percent, the amount of solvent in the polymer will be greater than that calculated based on the partial pressure of the solvent and simulating polymer as the heaviest component in the database.

There are techniques for dealing with this nonideality. Perhaps the best-known relationship dealing with the equilibrium between a polymer and solvent is the Flory-Huggins relationship. The use and limitations of this relationship are described in *Polymer Chemistry an Introduction* by Seymour and Carraher.

The Flory-Huggins relationship predicts the equilibrium of a solvent in the *noncrystalline* polymer phase. Equation (12-19) shows the original relation-

ship. The modification developed by the author is shown in equation (12-20).

The original Flory-Huggins relationship:

$$\ln(\text{PP}/\text{VP}) = \ln V_1 + (1 - M_1/M_2) * V_2 + U * V_2^2 \quad (12-19)$$

Where:

PP = the solvent partial pressure

VP = the vapor pressure of solvent

V1 = the volume fraction of solvent in polymer

V2 = the volume fraction of polymer

M1 = the molar volume of solvent, cc/g-mol

M2 = the molar volume of polymer, cc/g-mol

U = the interaction parameter between the solvent and the polymer

Manipulation and assumptions ($V_2 = 1$ and $M_1/M_2 = 0$) by the author of this book yields

$$\ln(\text{PP}/\text{VP}) = \ln(D_2 * X_1 / (D_1 * 1000000)) + 1 + U \quad (12-20)$$

Where:

D1 = the density of the solvent

D2 = the density of the polymer

X1 = the weight of the solvent in the polymer, ppm

The interaction parameter can be evaluated knowing the “solubility parameters”:

$$U = M_1 * (S_1 - S_2)^2 / (R * T) + Z \quad (12-21)$$

Where:

S1 = the solvent solubility parameter (cal/cm³)^{0.5}

S2 = the polymer solubility parameter (cal/cm³)^{0.5}

Z = the lattice constant. In theory = 0.35 ± 0.1

The values of solubility parameters are given in various handbooks. It should be emphasized that the concentrations of solvent in the polymer are that which exist in the noncrystalline region. The standard assumption is that there is no solvent in the crystalline region.

While this book cannot delve into all aspects of polymer–solvent equilibrium, the approach described above is meant to show that there are

techniques available to estimate the equilibrium as opposed to simulating a polymer as the heaviest component in the database. While there are computer simulations that allow prediction of a polymer–solvent equilibrium, the above analysis will be of value in understanding the basis for these simulations or in doing the simulation by manual calculation.

12.9 EXAMPLE PROBLEMS

The following example problems illustrate the application of these concepts. These are shown to illustrate the calculation approach. As such they are not formatted in the standard problem-solving technique proposed in this book.

12.10 EXAMPLE PROBLEM 12-1

A two-phase liquid mixture consisting of hexane and water is present in a process vessel at a pressure of 5 psig. The mixture enters the vessel at the boiling point. What is the boiling point of this mixture? The vapor from this drum must be dried to remove water. How could the amount of water present in the vapor phase be reduced below 0.26 mols per mol of hexane? The vapor pressure data in psia is given in Table 12-4.

Since there are two liquid phases present and the mixture is at the boiling point, equation (12-10) shown below provides the basis for the solution.

$$\Pi = VP_w + VP_{HC} \tag{12-10}$$

Where:

- Π = the total pressure of the two liquid phases
- VP_w = the vapor pressure of the water phase
- VP_{HC} = the vapor pressure of the hexane phase

Using the vapor pressures given earlier, the boiling point of the mixture can be determined as shown in Table 12-5.

Table 12-4 Vapor pressure data

	Temperature, °F					
	100	120	140	160	180	200
Component	Vapor Pressure, Psia					
Water	0.95	1.69	2.89	4.74	7.51	11.53
Hexane	5	7.79	11.02	15.4	22	28.7

Table 12-5 Boiling point estimate

	Temperature, °F			
	100	120	140	160
VP of water, psia	0.95	1.69	2.89	4.74
VP of hexane, psia	5	7.79	11.02	15.4
Total (Π), psia	5.95	9.48	13.91	20.14
Mols water/mol hexane	0.19	0.22	0.26	0.308

By interpolation, Π will equal 19.7 (5 psig + 14.7) when the temperature of the mixture is equal to 159°F. This by definition is the boiling point.

If the vessel were operated at a slight vacuum (<13.9 psia), the amount of water in the vapor would be below 0.26.

12.11 EXAMPLE PROBLEM 12-2

A vapor phase mixture at 200°F and 20 psia containing 50 mol percent water and 50 mol percent hexane flows into a cooler. Determine the following using the vapor pressures given in the previous problem:

- The temperature of the initial condensation and which component condenses first.
- The temperature at which the remaining component begins to condense.

The solution of this problem depends on utilizing the concepts discussed earlier. That is:

The partial pressure of a component can never exceed the vapor pressure of the component at the given temperature.

Mathematically this was expressed as:

$$\Pi * Y_i \leq VP_i \quad (12-13)$$

The partial pressure of both hexane and water is 10 psia since the vapor phase contains 50 mol percent of each component. As noted in equation (12-13), the vapor pressure must always be equal to or greater than the partial pressure. Since the mixture is being condensed, the vapor pressure and partial pressures will be equal. Interpolating the vapor pressures given earlier, it can be shown that a vapor pressure of 10 psia occurs at the temperatures shown in Table 12-6.

Since as the temperature is decreased, the condensation point of water occurs first, it will form the initial liquid phase and it will begin to condense

Table 12-6 Estimation of condensation point

Component	Temperature (°F) for a VP = 10 psia
Water	192
Hexane	134

Table 12-7 Estimation of condensation point of second phase

Component	Temperature, °F		
	120	140	160
Water, psia	1.69	2.89	4.74
Hexane, psia	7.79	11.02	15.4
Total, psia	9.48	13.91	20.14

at 192°F. It is important to recognize that the calculation shown above is valid only for finding the component that condenses first and the condensation point.

Hexane will not begin to condense until the total vapor pressure of the two liquid phases equals the total pressure (20 psia). This can be estimated as shown in Table 12-7.

Thus at a temperature of $\approx 160^\circ\text{F}$, sufficient hexane will condense to form a second phase. At this point (160°F), the vapor phase composition can be estimated from the vapor pressures by dividing the water vapor pressure by the hexane vapor pressure, which gives a composition of 0.308 mols of water per mol of hexane.

If a heat exchanger to do this condensation job were being designed, it would be split into different zones. From 200 to 192°F , there will be no condensation. This is a vapor cooling zone only. From 192 to 160°F , only water will condense. There will be trace amounts of hexane that condense as necessary to saturate the water phase with hexane. The vapor phase composition in this range can be estimated based on equation (12-22) as follows:

$$Y_w = VP_w / \Pi \quad (12-22)$$

Where:

Y_w = the mol fraction of water in the vapor phase

VP_w = the vapor pressure of water at the temperature of interest, psia

Π = the total pressure, psia

When a temperature of 160°F is reached, hexane will begin to condense. The temperature will remain at 160°F until all hexane and water are condensed. A condensation curve for this system is shown in Figure 12-3.

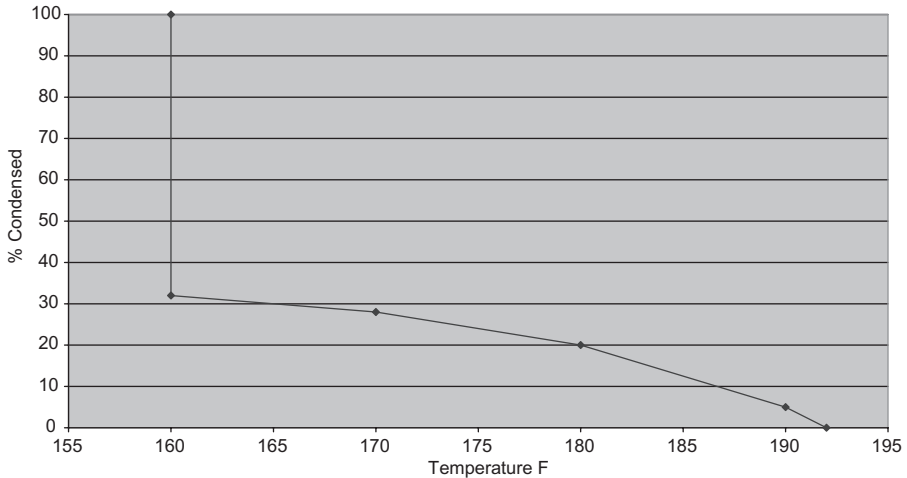


Figure 12-3 Percent condensation versus temperature.

12.12 EXAMPLE PROBLEM 12-3

Find the approximate relative volatility for water dissolved in propane at 70°F.

Given:

- Vapor pressures at 70°F:
 Water 0.363 psia
 Propane 118 psia
- Solubility of water in propane at 70°F, 0.016 lbs/100lbs propane

Calculations:

Converting the solubility to mol fraction gives 0.00039 mols of water/mol propane.

Since essentially all of the pressure on the system is due to propane:

$$\Pi = 118 \text{ psia}$$

Substituting in equation (12-9) gives the following results:

$$K = VP/(X \cdot \Pi) \quad (12-9)$$

$$K = 0.363/(0.00039 \cdot 118) \quad (12-23)$$

$$K = 7.88 \quad (12-24)$$

Since the equilibrium constant for propane is 1 (vapor pressure / total pressure), the relative volatility of water to propane is approximately 8. Thus, water would be more volatile than propane.

Chapter 12 Table of nomenclature

A_v	The activity of water in the vapor phase
A_w	The activity of water in the hydrocarbon phase if it is dissolved in the hydrocarbon
C	The number of components in the mixture
D_1	The density of the solvent
D_2	The density of the polymer
F	The degrees of freedom (temperature, pressure and composition)
K	The equilibrium concentration of the desired component. In this chapter, it is used in reference to a hydrocarbon or water dissolved in a hydrocarbon
k	The volatility of the <i>heavy key</i> relative to the <i>light key</i> . Note this will always be less than 1
L	The internal liquid rate in a fractionation tower, mols/hr
M_1	The molar volume of solvent, cc/g-mol
M_2	The molar volume of polymer, cc/g-mol
N	The number of theoretical trays in the rectification section
P	The number of phases present
PP	The partial pressure of the component under study
R	The internal liquid to vapor mol flow rate ratio in a fractionation tower
S_1	The solvent solubility parameter $(\text{cal}/\text{cm}^3)^{0.5}$
S_2	The polymer solubility parameter $(\text{cal}/\text{cm}^3)^{0.5}$
U	The interaction parameter between the solvent and the polymer
V	The internal vapor rate in a fractionation tower, mols/hr
V_1	The volume fraction of solvent in polymer
V_2	The volume fraction of polymer
VP	The vapor pressure of the component under study. In this chapter, it could be the vapor pressure of the hydrocarbon phase (VP_{HC}), the vapor pressure of the water phase (VP_w), the vapor pressure of the first component to condense (VP_i) or the vapor pressure of a solvent dissolved in a hydrocarbon (VP)
X	The concentration of a component in the liquid phase, mol fraction. As used in this chapter, it could be either the saturation concentration of water in hydrocarbon at the chosen temperature or the hydrocarbon concentration in a mixture

X_D	The composition of the heavy key in mol fraction in the overhead distillate product
X_N	The liquid phase composition of light key or heavy key on tray N, mol fraction
X_{N-1}	The liquid phase composition of light key or heavy key on tray above tray N, mol fraction
X_T	The composition of the heavy key in mol fraction at the start of the rectification section
X_1	The weight of the solvent in the polymer, ppm
Y	The concentration of a component in the vapor phase, mol fraction. It could be water (Y_W), hydrocarbon (Y_{HC}) or the composition of the first component in a hydrocarbon–water mixture to condense (Y_i)
Y_N	The vapor phase composition of light key or heavy key on tray N, mol fraction
Z	The lattice constant. In theory = 0.35 ± 0.1
σ	The relative volatility, light key to heavy key
Π	The total pressure

Light key refers to the component that is the most volatile. Heavy key refers to the component that is the least volatile

PUTTING IT ALTOGETHER

13.1 INTRODUCTION

The previous chapters have been focused on various phases of problem-solving procedures and activities, as well as process engineering calculation techniques. The actual procedures and techniques, which are applicable for any problem-solving activity, have been discussed. In addition, Chapters 6 through 12 contain experience-based process engineering calculation techniques and guidelines. In each of these chapters, there are example problems that are directed toward the theme of the particular chapter. In real life, problems don't come packaged so neatly. For example, what is described as a problem associated with a prime mover may well be a problem associated with a reactor.

In order to see how these areas fit together, several real-life example problems are discussed in this chapter. The chapter shows how the five-step problem-solving procedure (Chapter 3) can be used, how working hypotheses can be formulated (Chapter 5) and how various process engineering calculations (Chapter 6 through 12) can be utilized to develop and confirm these hypotheses.

13.2 DON'T FORGET TO USE FUNDAMENTALS

Two of the most powerful tools that a process engineer can use in problem solving are heat and material balances. The material balance simply states

that, with the exception of atomic power, mass cannot be created or destroyed. Thus, the total flow into a process or a unit operation must be equal to the total flow out. A comparable truism applies to heat balances. In addition to the need for a process to be in balance, heat and material balances can be used to determine unknowns. For example, material balance principles can be used to determine the production rate of a desirable or undesirable component. If an undesirable by-product is being produced in a reactor and removed in a purge stream, the rate of production is simply the removal rate. Heat balances can be used to determine the boil-up rate from the steam rate. A problem solver might well be told that a tower is flooding because the trays are plugged. When he performs a heat balance, he might well conclude that the heat input to the tower is less than the heat being removed from the tower. If he makes a closer examination, he might find that the problem really is a steam meter that is indicating a flow rate much less than actual flow. This is causing the tower to be flooded due to the excessive vapor rate being generated in the reboiler.

As will be noted in the example problems, knowing the flow rates of process or utility streams is a requirement for successful problem solving. While this may seem very basic, it is amazing how many problem solvers will start developing intricate hypotheses even though flow instruments indicate that the amount of material coming into the unit operation does not equal the amount of material leaving. Thus, one of the key things for a problem solver to remember is the idea of not forgetting the fundamentals of their discipline.

13.3 EXAMPLE PROBLEM 13-1: DO FUNDAMENTAL PROCESSES DEVELOPED IN THE UNITED STATES TRANSLATE TO EUROPE?

A chloride removal unit designed and operated in the United States was an integral part of a gas drying process that used Tri Ethylene Glycol (TEG) as the circulating drying solvent. Water was removed from the gas in the absorber using a stream of TEG that had a very low water content. The properties of TEG are such that water has a very low partial pressure when dissolved in the TEG. Thus, it can be readily used to dry gases of all descriptions.

In the drying process, the TEG leaving the absorber and containing the water removed in the absorber flowed to a heated two-stage regeneration system. In this regeneration system, the dissolved water was stripped from the gas and the dry TEG was recirculated to the absorber. The initial stage of the regeneration system was a heated flash step with about 5 minutes of residence time. The second stage was a vacuum distillation tower. The TEG from the vacuum distillation tower flowed back to the absorber.

The gas to be dried was a chlorine derivate. Some of the gas dissolved in the circulating TEG was converted to hydrogen chloride (HCl) as the solution was heated as part of the regeneration step. The reaction of the gas to form HCl was known to be first order with respect to the concentration of the

chlorine derivative in the circulating TEG. However, the exact reaction rate constant and Arrhenius constant were not known. Essentially all of this reaction occurred in the first stage flash drum of the two-stage regeneration system. This stage was operated at 175°F and 5 psig. The level in the drum was controlled so that the residence time was limited to 5 minutes. The second stage of the regeneration system consisted of a small vacuum fractionating tower. HCl generation in this stage was very limited because of the short residence time and low pressure.

The HCl formed was neutralized using a soluble amine. However, the amine could not be added continuously since the HCl-amine complex would build up in the circulating TEG to an unacceptably high level. The HCl was removed from the HCl-amine complex by passing a small stream of dry TEG through a drum filled with ion-exchange resin. Ion-exchange resins are complex salts supported on a synthetic resin such as polystyrene. This particular ion-exchange resin had the capability of removing the Cl^- ion and replacing it with an OH^- ion. Thus, HCl was converted to water. The ion-exchange resin itself was converted from an OH^- form to a Cl^- salt. As this process continued, the bed would eventually become saturated with Cl^- ions and become ineffective. To restore the bed, it was removed from service and regenerated using water and a sodium hydroxide solution. This regeneration was done whenever the concentration of chlorides in the outlet increased above 50 ppm. A simplified drawing of the process is shown in Figure 13-1.

The process was designed and installed in a location in the United States. After initial start-up problems, the operation of the process was very successful. The chlorides were controlled at a concentration of 500 ppm with a flow

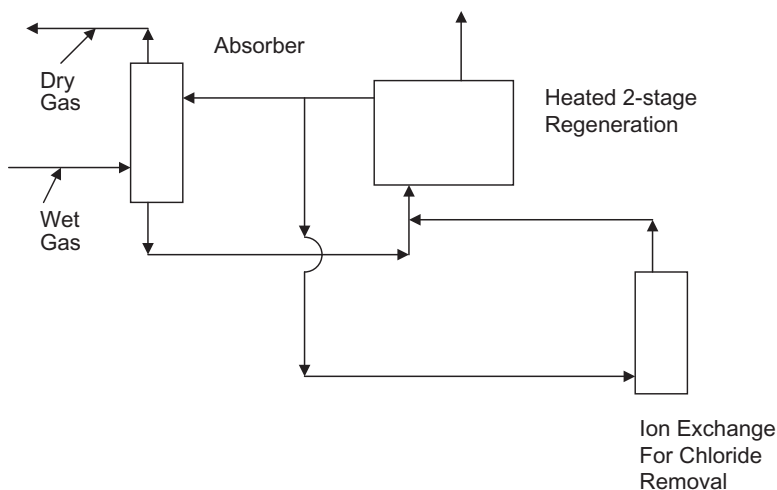


Figure 13-1 TEG system.

to the ion-exchange bed of 500lbs/hr. During the initial operations, high corrosion rates were encountered when the chloride level increased to 1000ppm.

An identical unit was installed in Europe. Flow rates, temperatures and pressures were all the same. While the gas was successfully dried, the concentrations of chlorides in the circulating TEG rose to 1500 ppm in a month after start-up. The ion-exchange bed appeared to be operating well since the outlet concentration from the bed was zero until the ion-exchange resin became saturated with chlorides. However, the bed had to be regenerated more frequently than anticipated due to the heavy loading of chlorides. At the time, the plant in Europe was not using the problem-finding concepts discussed in Chapters 3 and 5. Because of the concern over corrosion, European management shut the unit down. While significant corrosion had not yet been observed, they were convinced based on experience in the United States that high corrosion rates would be observed soon. After some preliminary problem-solving attempts on their own, they requested help from the original designer in the United States.

When the problem solver from the United States arrived on the scene, he began a methodical problem-solving activity using the approach discussed in the previous chapters. This methodical problem-solving approach was even more important in this case since there were significant geopolitical factors involved. There was a great deal of animosity between the European affiliate and the United States-based technical staff. The problem solver began the five-step approach as described in Chapter 3.

Step 1: *Verify that the Problem Actually Occurred*

Since operation at high chloride concentrations had not yet resulted in observable corrosion, the first problem to be verified was that the actual concentration of chlorides was as high as 1500 ppm. The laboratory procedure was confirmed and several samples were analyzed confirming that indeed the chloride concentration was 1500 ppm. Since the corrosion rate had been so severe in the United States at a chloride level of 1000 ppm, it did not seem wise to continue operation and simply monitor the corrosion rate.

The problem solver's next step in verifying that the problem actually occurred was to compare the theoretical chloride buildup to the actual chloride buildup in Europe. Since the reaction rate constant was not known, the theoretical chloride buildup was determined based on operations in the United States. Based on material balance principles, the problem solver calculated the chloride production rates in the United States. This material balance principle is as follows:

$$RC = F * X_F \quad (13-1)$$

Where:

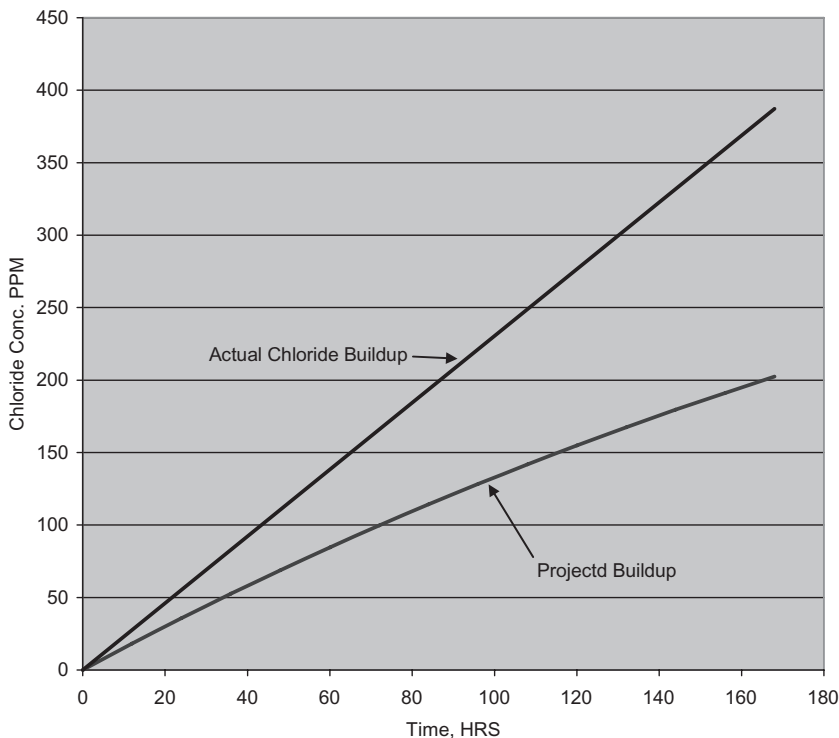


Figure 13-2 Actual and projected Cl buildup.

RC = the rate of chloride production in the United States, lbs/hr

F = the flow rate to the ion-exchange bed, lbs/hr

X_F = the concentration of chlorides in the flow to the ion-exchange bed, weight fraction

Note equation (13-1) assumes that the chloride concentration in the outlet from the ion-exchange bed was zero. This was true essentially all of the time.

Knowing the rate of chloride production in the United States and assuming that it was the same in Europe, the problem solver could then estimate the chloride concentration buildup rate in the European plant by knowing the TEG inventory. He then developed the relationships shown in Figure 13-2. In this figure, the projected chloride buildup based on kinetic relationships developed in the United States is shown, along with the actual chloride buildup. This provides a means of comparing the theoretical and actual chloride concentration buildup rates. Obviously there was a significant difference between the two rates.

Step 2: Write Out an Accurate Statement of What Problem You Are Trying to Solve

The problem solver wrote out the problem statement as follows:

“The chloride concentration in the circulating TEG in the European plant has built up to 1500 ppm instead of an anticipated level of 500 ppm. This is a major concern because experience in the United States indicated that significant corrosion would begin at levels above 1000 ppm. This high level of chlorides is being experienced in Europe at the apparent same identical process conditions used in the United States which resulted in a chloride level of only 500 ppm. An analysis of the rate of chloride buildup indicates that the higher chloride production rate has been present since the start-up of the equipment in Europe. Determine why the chloride concentration in the circulating TEG has built up to 1500 ppm instead of an anticipated level of 500 ppm. In addition to understanding what is causing the high level, changes to reduce the steady-state concentration to 500 ppm should be recommended.”

Step 3: Develop a Theoretically Sound Working Hypothesis that Explains the Problem

The question list given in Chapter 5 was used as a guide to develop potential working hypotheses. A summary of this analysis is shown in Table 13-1.

The value of using a list similar to Table 13-1 is that it helps to eliminate superfluous hypotheses that might be suggested and it allows focusing in on the likely areas for development of working hypotheses. For example, an examination of this table indicates that areas such as mechanical wear, fluid leakage or changes in operating conditions are unlikely routes to pursue. In addition, the most obvious conclusion—“the ion-exchange resin is not working” is shown by Table 13-1 to be highly unlikely. On the other hand, meter errors, higher than expected HCl production rates and design improvements in the regeneration area appear to be valuable areas to pursue. As is often the case in industrial problem solving, there may be more than a single item that is causing the problem. For this reason, the problem solver began looking in detail at the design improvements, the variables that might cause the reaction rate to form HCl to be higher than anticipated, and the difference in a venturi meter and orifice meter in the specific application. It was not possible to isolate the potential areas of flowmeter error and higher than anticipated HCl production rate because the technique for calculating HCl production rate depended on the flow rate of TEG to the ion-exchange bed. If this flowmeter were in error, the calculated HCl production rate would be in error. Thus, both possibilities had to be considered.

Since the operating conditions (temperature and pressure) were identical to those in the United States, it would appear that the rate of HCl generation would be the same. However as indicated earlier, the possibility of higher rates of HCl generation could not be eliminated. Since essentially all of the HCl

Table 13-1 Questions/comments for Problem 13-1

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed.
Are all instruments correct?	The instruments had allegedly been calibrated. However, it was observed that a venturi meter was being used in Europe where an orifice meter was used in the United States.
Are laboratory results correct?	All appeared to be correct.
Were there any errors made in the original design?	The design was essentially the same as that in the United States with the exception of improvements in the regeneration section.
Were there changes in operating conditions?	No. In fact, the operating conditions of temperature and pressure were identical to those used in the United States.
Is fluid leakage occurring?	This would not explain the problem.
Has there been mechanical wear that would explain the problem?	No.
Is the reaction rate as anticipated?	Higher rates of HCl formation could explain part of the problem. On the other hand, the ion-exchange bed appeared to be performing as designed except for the frequent regenerations. The frequent regenerations appeared to be associated with the higher than anticipated rate of HCl formation.
Are there adverse reactions occurring?	There were no unusual reactions that could explain the problem.
Were there errors made in the construction of the process?	Since the unit had only recently been built, this had to be considered.

was produced in the first stage flash drum, the problem solver began an analysis of that operation. Referring back to Chapter 8, the kinetic relationship can be expressed in terms of reaction rate as shown below:

$$R^* = C^*DF \quad (13-2)$$

Where:

R^* = the rate of change with time per unit volume of the compound under study, mols of HCl/ft³-minute that are formed

C = a constant referred to as the “lumped parameter constant”

DF = the driving force or incentive for reaction to occur, mols of chlorine derivative gas absorbed/ft³ of TEG. Since as indicated earlier essentially all of the HCl generation occurred in the flash drum that was the only area to be considered

In this case, the constant is the reaction rate for the formation of HCl from the chlorine derivative gas. This will be a function of temperature only. As indicated, the driving force will be the concentration of the gas in the TEG in the flash drum. This will depend on temperature and pressure only. Thus, the driving force and lumped parameter constant should be the same in Europe and the United States. This means that “R”, which is the rate of HCl formation in mols per minute per unit of volume, should be the same. Thus, if the absolute value of HCl formation in mols/hr is higher, it can only be due to an increase in drum volume or residence time at a constant flow rate. This possibility by itself does not provide enough data to formulate a hypothesis. In order to determine if there is a valid working hypothesis related to increased drum volume, the following items were reviewed:

- The dimensions of the first stage flash drum were reviewed and it was concluded that the dimensions were identical in Europe and the United States.
- While the measured liquid levels in the drums were both held at 20 percent, the ranges of the liquid level instruments were different. This was discovered only during a detailed review of the instrument specification sheets. The instrumentation philosophy in the United States was to only cover the planned range of operations with the liquid level instrument. This would provide a higher degree of accuracy. The range of the level instrument was 50 inches. In Europe, the philosophy was to cover the entire height of the drum or 75 inches in this case. The Europeans considered this to be a significant design improvement.

Thus, the absolute liquid level in Europe was 15 inches versus 10 inches in the United States. Since the drums were of the same diameter and the flow rates were identical, this difference would provide 50 percent more reaction volume in Europe than in the United States. This would increase the HCl production by 50 percent.

In order to determine whether this hypothesis would explain all of the apparent increase in HCl production observed in Europe, an HCl material balance was developed for Europe in a similar fashion to that done for the United States. The premise of these balances was that the HCl removed was equal to the HCl produced. These balances are shown in Table 13-2.

Thus, it appeared that a working hypothesis that the increased residence time was responsible for an increased amount of chloride produced would be a valid working hypothesis. However, the calculated chloride production rate was only about half of the value obtained by material balance (0.38 lbs/hr

Table 13-2 Chloride balances

Variable	United States (base case)	Europe
Flow rate to ion exchange, lbs/hr	500	500
Chloride concentration into ion exchange, ppm	500	1500
Chloride concentration out of ion exchange, ppm	0	0
Chloride production by material balance, lbs/hr	0.25	0.75
Calculated chloride production ⁽¹⁾ , lbs/hr	0.25	0.38

(1) The calculated chloride production rate was set at the material balance level for the base case (United States) and was increased by 50 percent to allow for the increased residence time in Europe.

versus 0.75 lbs/hr). The failure to get a good material balance calculation check indicated that there might be other problems. Thus, rather than proposing a plant test of lowering the level in the first stage flash drum, the problem solver began considering other possible problems.

A review of the question guidelines and answers in Table 13-1 indicated that there was likely some construction mistake or mistake in the revised design. Several possible additional hypotheses were developed. Most of them tended to point to the flow measurement of the stream going to the ion-exchange bed. If the flow rate was significantly less than indicated, chlorides would still be removed, but the concentration would build up to a higher level than would be anticipated. For example, if the flow was actually 250 lbs/hr, then the amount of chloride removed in the ion-exchange unit would be equivalent to that calculated based on the increased residence in the first stage flash drum. The problem solver began developing a hypothesis associated with the flowmeter by selecting the simplest explanation possible. A review of the venturi meter calculations used for the flow to the ion-exchange bed indicated that it was selected to minimize pressure drop. The venturi meter discharge coefficient was assumed to be 1, which would have been true for a low-viscosity fluid. However, the TEG has a viscosity much higher than a typical hydrocarbon. While it appeared to the problem solver that a standard orifice meter would have provided a much more accurate installation, he refrained from indicating this to the Europeans.

The problem solver now developed the following hypothesis that actually contained two possible theoretically correct working hypotheses.

“It is believed that the increased absolute level in the flash drum (15 inches versus 10 inches) is causing the chloride production to be 50 percent higher in Europe than in the United States. The level hypothesis does not explain that the concentration of chlorides in the TEG is three times that anticipated based on results in the United States. Thus, another problem must be present. It is believed that the measurement of flow to the ion-exchange bed is in error.”

It should be noted that this problem illustrates that in industrial problem solving, there are often more than one valid hypothesis. Using basic chemical engineering principles can often confirm whether one hypothesis can explain the entire problem.

Step 4: Provide a Mechanism to Test the Hypothesis

Two separate plant tests were developed to test both of these hypotheses. The tests were conducted concurrently since as conceived there was no interaction between the two tests. In the first test, the level was reduced in the first stage flash drum so that the residence time was reduced to 5 minutes. In the second test, the flow to the ion-exchange bed was diverted into a 5-gallon bucket and the actual flow rate was measured. The 5-gallon bucket required about 11 minutes to fill as opposed to the 6 minutes that it would have required if the flow rate was really 500 lbs/hr. In order to confirm that the problem was truly solved, the plant test on the flash drum was continued. That is, the operating directive for the level was set so that the residence time continued at 5 minutes. In addition, the flow rate to the ion-exchange bed was increased to a *measured* value of 1000 lbs/hr. It was anticipated that a measured flow of 1000 lbs/hr would give an actual flow of 500 lbs/hr. The flow was again measured using the 5-gallon bucket to confirm that a flow rate of about 500 lbs/hr was achieved. After a few days at these conditions, the chloride concentration decreased to 500 ppm, the concentration experienced in the United States.

Step 5: Recommend Remedial Action to Eliminate the Problem without Creating Another Problem

The remedial action was relatively simple and consisted of only slight modifications to the changes made to conduct the plant test. These changes were designed to ensure that at a future time comparisons made between the two plants did not cause changes in operations, which would recreate the start-up problems. The changes were as follows:

- The level instrument on the first stage flash drum was re-ranged from 75 to 50 inches. This would allow both flash drums in the United States and Europe to operate at the same apparent level (20 percent). This would also be the same absolute level of 10 inches. If the level instrument had not been re-ranged, it would have been necessary to maintain the level in Europe at about 13 percent. There was a concern that this discrepancy between the United States and Europe might lead the European affiliate to raise the flash drum level at some point to be consistent with the level in the United States.

- The discharge coefficient for the European venturi flowmeter was changed to a value that was based on the actual viscosity rather than an assumed value of unity.

A detailed potential problem analysis did not reveal any significant new problems if these changes were made.

13.4 LESSONS LEARNED

If the problem-solving concepts discussed earlier had been applied, the European technical staff might well have elected to predict the chloride buildup rate based on data from the United States. If they had been using this potential problem analysis concept, they would have been able to spot the problem much sooner than a month after start-up. As can be seen from Figure 13-2, it was readily apparent after 2 to 3 days that the chloride level was increasing much faster than would have been projected based on experience in the United States. The advantage of comparing the actual to projected chloride buildup is that problem-solving activity could have started 3 weeks earlier than actually experienced.

This problem illustrates the validity of calculations. There will always be a tendency to treat the first discovery as the root cause of the problem. Many industrial problems have more than a single root cause. For example, the discovery that the flash drum in Europe had more residence time than the comparable drum in the United States might have been considered the single root cause of the problem. If the problem solver had not concluded based on calculations that there must be another cause, the flash drum changes would have been made, but the problem of high chlorides would have continued. In the case described, it was especially desirable to insure that the problem solutions were complete since the problem solver had only a limited amount of time in Europe.

In our advanced age of electronic equipment, we often forget the more basic measurement techniques. The use of a 5-gallon bucket to measure the low flow rate of a low toxicity and nonvolatile material is probably one of the best techniques available.

Any design change regardless of how small (use of venturi meter and change in range of a level instrument) should receive a careful review including a potential problem analysis.

13.5 EXAMPLE PROBLEM 13-2: AN EMBARRASSING MOMENT

A high vacuum system was designed as part of a new process. The vacuum system was required to achieve an absolute pressure of 15 mm of Hg. In order

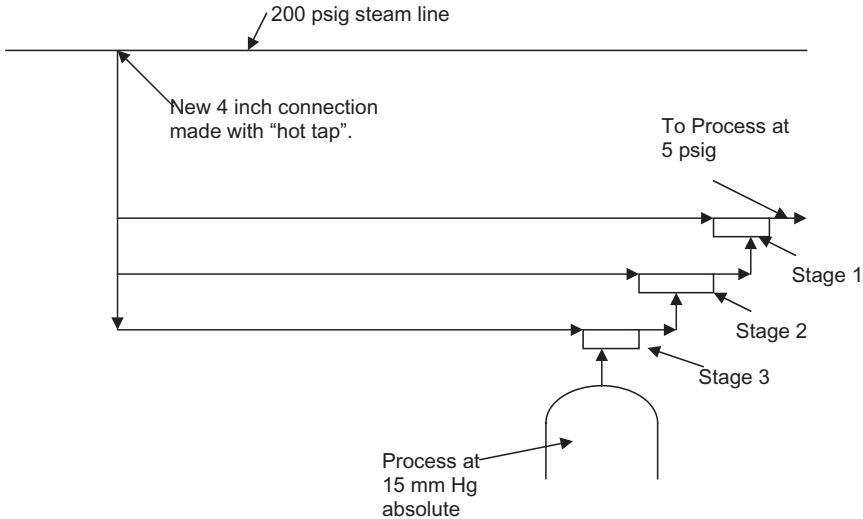


Figure 13-3 Schematic of three-stage steam ejector.

to do this, a three-stage steam ejector was selected. A schematic of the vacuum system is shown below in Figure 13-3.

The construction was relatively straightforward except for obtaining a steam supply for the ejector. In order to furnish steam and avoid a shutdown of the 200-psig steam supply line, it was necessary to “hot tap” the steam line. Hot tapping is a procedure where a valve with a flange is welded to the line. When the valve is fully secured and the welding is inspected, a cutting instrument is connected to the open end of the flanged valve. The valve is opened and the cutting instrument is lowered into the valve opening until it touches the pipe. A small pilot drill is first used to cut a small (1/4 to 3/8 inch) hole. Following that, a full size hole is cut. The tool used to cut the full size hole is then used to pull the piece of the pipe that has been cut out back through the valve. The valve is closed as the tool is removed. The new steam piping to the process is then connected to the valve. The valve is then opened at the appropriate point in the start-up procedure. The hot tap crew will often save the section of pipe cut from the main line as proof that the hot tap really had been made.

The start-up procedure for the three-stage ejector system called for starting the stages in the order shown on the schematic drawing. This allowed the lowest steam demand stages to be started first. The steam jet manufacturer’s guaranteed steam consumptions were as follows:

- Stage 1 300 lbs/hr
- Stage 2 500 lbs/hr
- Stage 3 1700 lbs/hr

The start-up procedure seemed to go well as the first and second stage jets were placed into service. The steam pressure as measured by a gauge in the new 4-inch steam line remained relatively constant at about 200 psig and the pressure in the vacuum drum decreased to the level anticipated with only two stages in service. However, when steam flow was started to the third stage, the measured steam pressure on the 4-inch line decreased rapidly to 105 psig, and the pressure on the vacuum drum increased as the first and second stage jets were no longer able to perform at the reduced steam pressure. The initial reaction of the problem solver was that there was obviously something wrong with the third stage jet. After all, the system performed perfectly when only two stages were used. He called the sales representative and strongly suggested to him that maybe an orifice had been left out of the third stage jet. The problem solver believed that this would cause a huge increase in steam flow and result in a large pressure drop in the 4-inch line. As time passed, the problem solver began a more methodical approach to analyzing the problem. He used the five-step approach as follows:

Step 1: *Verify that the Problem Actually Occurred*

There was little doubt that the problem occurred. The dropping in steam pressure and the loss of vacuum were also accompanied by loud noises inside the drum as material flowed backwards through the ejectors. However, to satisfy the need to verify the problem and get a maximum amount of data, the start-up was repeated. The same results were observed. However, the increased attention to the steam pressure gauge on the 4-inch line indicated that the steam pressure actually dropped slightly when the first and second stage ejectors were placed into service.

Step 2: *Write Out an Accurate Statement of What Problem You Are Trying to Solve*

The problem solver developed a problem statement as follows:

“During start-up of the steam jet system, the steam pressure on the 4-inch steam supply line decreased rapidly to 105 psig when the third stage ejector was placed into service. The operation of the three-stage steam jet is impossible at this low pressure. Very small pressure drops were also observed as the first and second stage ejectors were placed into service. The same results occurred during both instances when the ejector system was being placed into service. The pressure on the 200-psig steam pressure header was normal during both trials. There are no steam meters available to measure the actual steam flow to the ejector system. Determine why the steam pressure on the 4-inch steam supply line decreased rapidly to 105 psig when the third stage ejector was placed into service. Recommendations for modifications to allow operating the steam ejector system are also to be provided.”

Table 13-3 Steam pressure measurements

Ejectors in Service	Steam Pressure, Psig
0	200
1	198.5
2	190.3
3	105

Table 13-4 Questions/comments for Problem 13-2

Question	Comment
Are all operating directives and procedures being followed?	The vendor provided start-up procedure that was being followed exactly.
Are all instruments correct?	The pressure gauge that was initially used was replaced with a new gauge before the second test.
Are laboratory results correct?	Not applicable in this case.
Were there any errors made in the original design?	The 4-inch steam line could be too small.
Were there changes in operating conditions?	No. The process was being operated exactly as specified on the duty specification for the steam ejector.
Is fluid leakage occurring?	Not applicable.
Has there been mechanical wear that would explain the problem?	Not applicable.
Is the reaction rate as anticipated?	Not applicable.
Are there adverse reactions occurring?	Not applicable.
Were there errors made in the construction of the process?	Since the unit had only recently been built, this had to be considered.

The actual measured pressures from the second trial are shown in Table 13-3.

Step 3: Develop a *Theoretically Sound Working Hypothesis that Explains the Problem*

The question list given in Chapter 5 was used as a guide to develop potential working hypotheses. A summary of this analysis is shown in Table 13-4.

The approach of using the guidelines provided by Chapter 5 may seem trivial for this example, but they helped to isolate the development of a hypothesis to two areas. The areas that the problem solver decided to investigate further were the sizing of the 4-inch steam supply line and some sort of construction error. The hypothesis of a construction error would also include the possibility of an error in the manufacturing of the steam ejector. Three potential working hypotheses were proposed as described below:

1. The process designer had made a mistake in the sizing of the 4-inch steam supply line.
2. There was an error made in the construction of the third stage steam jet.
3. The hot tap crew had made an error and did not completely cut and remove the 4-inch piece of the line.

Initially the hot tap crew was contacted to ascertain that they did pull a piece of pipe from their cut to determine that the hot tap had indeed been completed. Unfortunately, this was many weeks after the cut was made and the problem solver was told that all cuts made during that time frame had been discarded.

In order to narrow down the possible number of working hypotheses to a minimum, the following actions were taken and the indicated results obtained:

- The steam supply line was resized and it was concluded that the 4-inch line was more than adequate. The pressure drop should be less than 2 psi even if the steam rates were double the rates guaranteed by the steam jet manufacturer.
- The third stage jet was removed and inspected and the dimensions were compared to the factory-issued drawings. The dimensions of the ejector were as specified in the drawings.

The only remaining hypothesis was that the hot tap had not been completely cut through and that all of the steam was flowing through the pilot drill hole or another restriction in the piping.

Step 4: Provide a Mechanism to Test the Hypothesis

While the hypothesis could have been tested by insisting that the hot tap crew return and redo their hot tap, the problem solver decided to test the hypothesis by using calculations. He proceeded to consider the data shown in Table 13-5.

If the “hot tap” had not been cut completely, the pressure drop across the pilot drill hole should be proportional to the steam flow rate squared. Thus, he decided to plot the pressure drop versus the flow rate squared. The resulting plot is shown in Figure 13-4.

The resulting plot had a slope of 0.0000152 and an intercept of zero. Thus, it could be specified by the following relationship:

$$\Delta P = 0.0000152 * F^2 \quad (13-3)$$

Where:

Table 13-5 Steam flow and pressure drops

Stages in Service	Steam Flow, lbs/hr ⁽¹⁾	Pressure Drop, psi
1	300	2
2	800	10
3	2500	95

(1) The steam flows were taken from the steam jet manufacturer’s specification sheet.

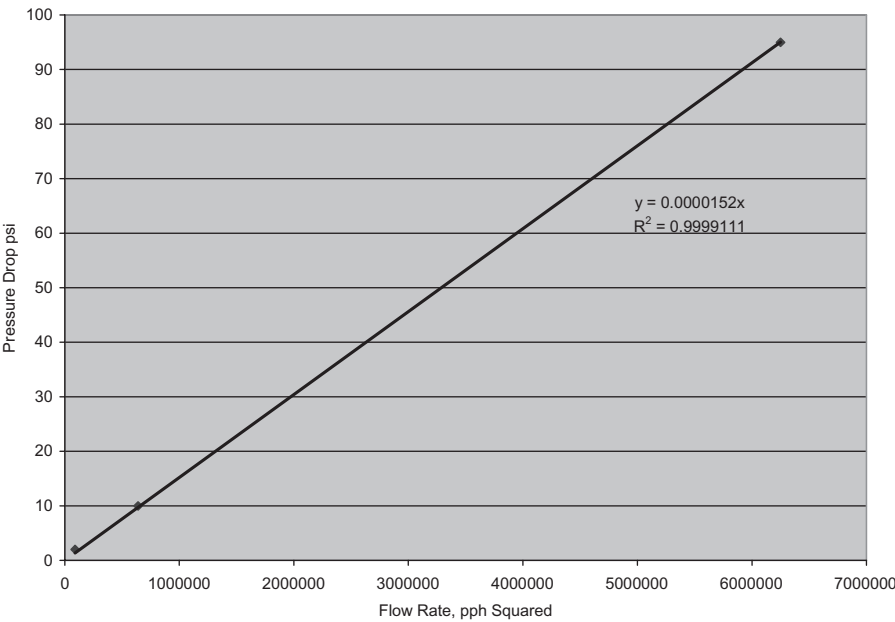


Figure 13-4 Pressure drop versus flow rate squared.

ΔP = the pressure drop across the restriction, psi
 F = the steam rate, lbs/hr

The intercept of zero was as expected. That is, at no flow there should be no pressure drop. The slope of 0.0000152 was used to approximate the size of the opening that steam was flowing through. To do this, the problem solver used the following relationship for fluid flowing through a restriction.

$$\Delta P = 0.5 * S * U^2 / 148.2 \tag{13-4}$$

Where:

S = the density of the flowing fluid relative to water
 U = the velocity of the flowing fluid through the orifice, fps

The constants represent conversion factors and the orifice discharge coefficient.

Since there was now an experimental relationship between the flow rate and the pressure drop, as well as a similar theoretical relationship, these two equations could be used to estimate the diameter of the restriction. To make this estimate, the right-hand side (RHS) values of equations (13-3) and (13-4) were set equal to each other since they were both equal to the pressure drop in the restriction.

$$0.0000152 * R^2 = 0.5 * S * U^2 / 148.2 \quad (13-5)$$

Knowing:

$$U = R / (3600 * A * \rho) \quad (13-6)$$

$$S = p / 62.4 \quad (13-7)$$

Where:

A = area of restriction, ft²

ρ = fluid density, lbs/ft³

Solving these two relationships for the area of the restriction and then calculating the resulting diameter gave a value of 3/8 inch. This was likely the diameter of the pilot drill used for the hot tap of the steam line.

It appeared likely that the hot tap had not been cut all the way through and that steam was only flowing through the opening that was cut for the pilot drill. When the hot tap crew was contacted, they agreed to return to recut the hot tap only after considerable discussion. When they did recut the hole, they were surprised to find that the piece of material that they removed was exactly as calculated by the problem solver. That is, it was a 4-inch piece of metal with a 3/8-inch hole in it.

Step 5: Recommend Remedial Action to Eliminate the Problem without Creating Another Problem

No additional actions appeared to be required after the hot tap was recut. The steam ejector system was started up successfully and the steam pressure on the 4-inch supply header remained constant at 200 psig throughout the start-up and operation.

13.6 LESSONS LEARNED

This problem illustrates how “jumping to conclusions” can often lead to embarrassing moments. Rather than immediately confronting the sales repre-

sentative, the problem solver should have made a careful study of the available data. A careful study of the data would have revealed that the steam supply pressure did not stay constant even when the smaller first and second stage jets were placed into service. The problem also illustrates the value of doing calculations to attempt to pinpoint the problem source. After the designer had rechecked the sizing calculations for the 4-inch steam line, the calculations described in Step 4 should have been done. If these additional calculations had been done, there would have been no reason to open and check the dimensions in the third stage jet. The removal of this third stage jet was a major effort since it was located three levels up in the structure and had large pipes connected to it.

The calculations described in Step 4 would have been sufficient to point out clearly that the “hot tap” was likely done incorrectly and thus would have eliminated the need to remove and inspect the third stage jet. These calculations also provided a strong argument for redoing the “hot tap” as opposed to just a suspicion that it was not done correctly.

13.7 EXAMPLE PROBLEM 13-3: PRIME MOVER PROBLEMS ARE NOT ALWAYS WHAT THEY APPEAR TO BE

An ethylene refrigeration system was expanded by increasing the capacity of a blower. Prior to the expansion, this blower was used to boost the pressure on the system from 10 inches of vacuum to 8 psig. The system was expanded by increasing the blower discharge pressure (also the compressor suction pressure) to 10 psig. The increase in pressure to 10 psig was to provide an increase in capacity of about 10 percent. No other changes were required in the ethylene compression or condensation system. The increased capacity of the blower was to be obtained by replacing the existing impeller with a larger impeller. This increase in impeller size would allow an increased flow rate and an increase in discharge pressure to 10 psig. A short shutdown was required in order to install the new impeller. A schematic drawing of the process is shown in Figure 13-5.

Ethylene liquid flows from the compression and condensation block to provide refrigeration for a low-temperature process operating at approximately -150°F . The ethylene liquid is vaporized at 10" of mercury vacuum and flows as vapor to the ethylene blower. Prior to the blower, a series of economizers (heat exchangers) raise the temperature of the ethylene from about -156 to -40°F . The blower boosts the pressure from 10" vacuum to 10 psig. The ethylene gas at 10 psig flows to the reciprocating compression system where it is compressed to approximately 350 psig and condensed in heat exchangers that are cooled by vaporizing propane. The refrigeration load is not constant. The rate of vapors flowing to the ethylene blower and compressors varies significantly. To maintain the suction pressure of the blower and compressor constant, “kickback valves” are provided. As the refrigeration

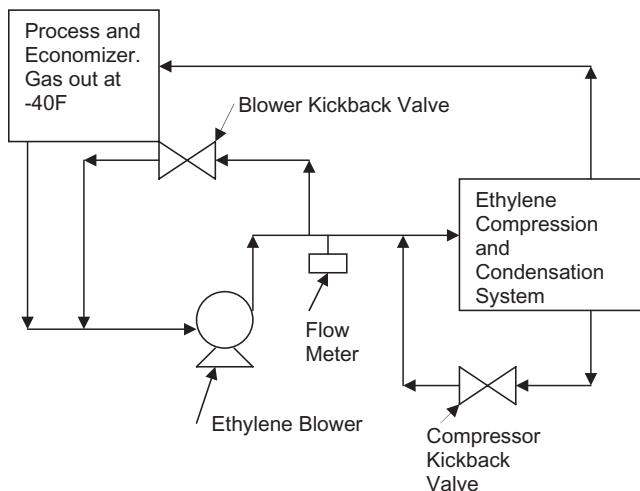


Figure 13-5 Ethylene refrigeration schematic.

load decreases, the kickback valves open keeping the suction pressures constant.

The operation of the expanded blower was disappointing. While it appeared that additional ethylene flow was obtained, the pressure was well below the required discharge pressure of 10 psig. Since ethylene flowed from the blower discharge to the compressor suction, this lower discharge pressure also resulted in a lower compressor suction pressure. The lower suction pressure caused both a reduction in compressor capacity and an increase in the compression ratio. Operations personnel requested technical help because in their words “This new impeller is not as good as the one that we took out!! We never had this kind of trouble before and that kickback valve was always open at least 10 percent.” The problem solver used the five-step approach to assess the situation.

Step 1: *Verify that the Problem Actually Occurred*

The verification that there was a problem was relatively easy. When attempts were made to increase the unit production and hence the refrigeration load above that possible before the new impeller was installed, the blower kickback valve would go all the way closed and the blower suction pressure would increase above the operating value of 10 inches of vacuum. Since operating at 10 inches of vacuum was necessary in order to maintain the process temperatures, the blower discharge pressure was reduced, causing the reciprocating compressors to have less than the desired capacity.

Step 2: Write Out an *Accurate Statement of What Problem You Are Trying to Solve*

Prior to attempting to write out an accurate problem statement, the problem solver decided to look at the blower manufacturer's supplied compressor curve for the new impeller. As part of the preparation for this assessment of comparing the theoretical blower curve to actual performance, he had all the key meters checked. So he knew that the blower suction pressure, discharge pressure and flow rate variables were as accurate as possible. In order to assess the blower performance, it was necessary to maintain the kickback valve in the closed position during the test. This was because the flowmeter was located outside the kickback valve line as shown in Figure 13-5. The problem statement that he developed was:

"The performance of the ethylene blower seems to be less than anticipated with the new impeller. Rather than obtaining a 10 percent to 12 percent improvement in the plant capacity, operations since the start-up of the revised facilities have resulted in a capacity only slightly above the previous capacity. While no test data exists for performance with the old impeller, operations personnel believe that the performance was adequate when the old impeller was being utilized. They also indicate that the kickback valve was normally open at least 10 percent. Currently, the valve is closed whenever the system is fully loaded. The ethylene compressors are operating as predicted. The problem is not related to instrumentation since all the meters have been checked. Determine the following:

- Is the blower operating as specified by the manufacturer's supplied blower curve?
- If it is not, determine why.
- Recommend changes to correct the problem or operating conditions that will allow operation at full capacity."

As indicated in Chapter 3, time is always an important component of a problem statement. In this problem while no data were available from past operations, the problem solver still noted that performance seemed adequate with the old impeller. In addition, he indicated that the problem seemed to have been present since the start-up of the expanded facilities. This helps to focus on the time period after the facilities were expanded. In parallel with developing working hypotheses, the problem solver decided to run a series of plant tests to assess the actual blower performance. A summary of these plant tests is shown in Table 13-6. In addition, the results are shown graphically in Figure 13-6.

Also note in the problem specification that the problem solver takes into account the operator's observations that prior to the expansion, the performance was adequate and that the kickback valve was open at least 10 percent essentially all of the time. **HOWEVER**, the problem statement did not include their conclusion that the blower was performing better with the old impeller.

Table 13-6 Blower capacity tests

Variable	Design	Test 1	Test 2
Molecular weight	28	28	28
Specific heat ratio	1.25	1.25	1.25
Gas compressibility	1	1	1
Polytropic efficiency, percent	70	TBD	TBD
Suction pressure, "Hg	10	7.5	8.7
Discharge pressure, psig	10	10	10
Gas density at suction, lbs/ft ³	0.0609	0.0670	0.0633
Flow rate, lbs/hr	35000	42590	36560
ACFM	9580	10590	9630
Temperatures			
Out economizer, °F	-40	-40	-40
Blower suction, °F	-40	-30.5	-29.3
Blower discharge, °F	87	81	91
Blower speed, rpm	10000	10000	10000
Calculated polytropic head, ft	24560	21525	23250
Projected polytropic head, ft		23200	24500
Performance deficiency, percent		7.2	5.1

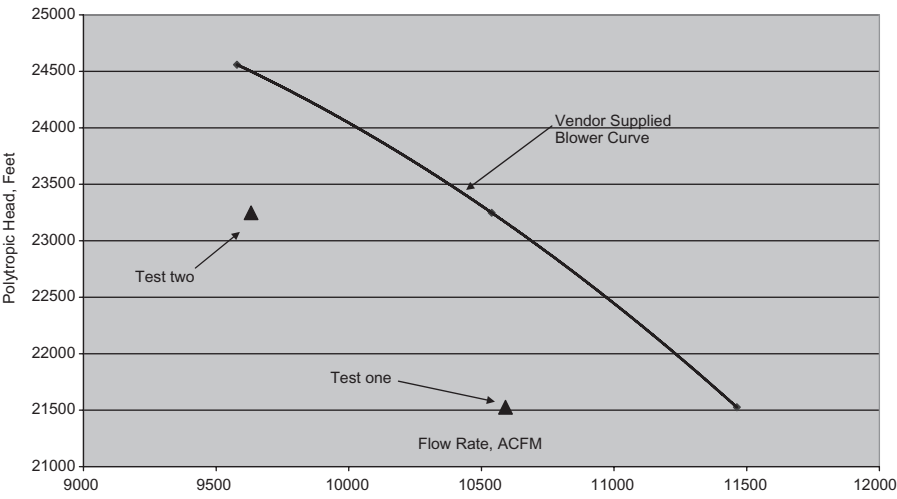


Figure 13-6 Blower capacity curve.

The polytropic head is calculated using the following equation given in Chapter 6:

$$H = 1545 * T_s * Z * (R^\sigma - 1) / M\sigma \quad (6-6)$$

Where:

- H = the polytropic or adiabatic head, feet
- T_s = the suction temperature, °R
- Z = the average (suction and discharge) compressibility
- R = the compression ratio
- M = the gas molecular weight
- σ = the polytropic or adiabatic compression exponent

The projected polytropic head is taken from the blower manufacturer's supplied head curve shown in Figure 13-6. The performance deficiency is simply the deviation from the projected head curve expressed as a percentage.

Figure 13-6 clearly indicates that the blower does not appear to be performing as predicted by the performance curve. However, this data does not by itself provide a working hypothesis. For example, if one simply presents a working hypothesis that says—"The blower is not performing as predicted by the blower manufacturer's supplied capacity curve", does this mean that the blower should be shut down for maintenance or is there another problem that is causing the blower to appear to be operating different than predicted by the performance curve?

Step 3: Develop a *Theoretically Sound Working Hypothesis that Explains the Problem*

The question list given in Chapter 5 was used as a guide to develop potential working hypotheses. A summary of this analysis is shown in Table 13-7.

Using these questions from Chapter 5, several hypotheses were developed as follows:

- There could have been errors in the design calculations for the new compressor impeller. This could consist of either errors in the data supplied to the manufacturer or errors made by the manufacturer.
- The wrong size impeller could have been installed.
- The increase in the blower discharge pressure could result in more leakage through wear rings.
- The increase in the blower discharge pressure could cause more leakage through the blower kickback valve.

Table 13-7 Questions/comments for Problem 13-3

Question	Comment
Are all operating directives and procedures being followed?	Operating directives were being followed exactly.
Are all instruments correct?	All instruments were checked.
Are laboratory results correct?	Not applicable in this case.
Were there any errors made in the original design?	There could be errors in the compressor impeller design calculations.
Were there changes in operating conditions?	Yes. The blower discharge pressure was increased as part of the revised design.
Is fluid leakage occurring?	Fluid leakage could be occurring through the kickback valve or through blower internals.
Has there been mechanical wear that would explain the problem?	Blower wear rings are a potential problem.
Is the reaction rate as anticipated?	Not applicable.
Are there adverse reactions occurring?	Not applicable.
Were there errors made in the construction of the process?	Since the unit had only recently been expanded, this had to be considered.

- The poor insulation on the line between the economizer and the blower suction could cause the ethylene to warm up and thus is causing a loss in capacity. As shown in Table 13-6, the gas temperature is increasing from -40°F to about -30°F .

All of these are possible hypotheses. The problem solver felt like with additional data and/or calculations that he could eliminate some of them. So he reviewed the original physical properties and design bases and confirmed that they were correct. He then reviewed the purchase order and blower manufacturer's specification for the new impeller and compared them to the bases for the upgraded blower. He found that these were consistent. Of course this does not eliminate the possibility that the wrong impeller was shipped from the supplier. He also compared the old blower curve to the new blower curve and found that they were consistent. That is, when extrapolating from the old blower curve to the new blower curve using the appropriate diameter scaling factors, the extrapolated blower curve was essentially the same as the one supplied by the blower manufacturer. Based on this work, he believed that he had done all that he could do except recommend a blower shutdown to eliminate hypothesis number 1. Before recommending that the blower be shut down to inspect the impeller to confirm that it was the correct diameter, he decided to consider the other hypotheses.

If there was internal leakage due to excessive clearance inside the blower, the internal gas recirculation would cause a decrease in the polytropic efficiency. This could be determined by the blower suction and discharge tem-

Table 13-8 *Calculated efficiencies for test runs*

	Test 1	Test 2
Suction temperature, °R	429.5	430.8
Discharge temperature, °R	541.0	551.1
Compression ratio	2.24	2.37
Compression exponent	0.286	0.285
Polytropic efficiency, percent	70	70.2

Table 13-9 *Calculation results*

	Test 1	Test 2
Gas rate, ACFM	10590	9630
Polytropic head at suction temperature, feet	21525	23250
Calculated polytropic head at -40°F	21050	22700

peratures. The following equations from Chapter 6 were used to estimate the efficiency for the two tests. The results are shown in Table 13-8.

$$\sigma = (k - 1) * 100 / (k * E) \quad (6-7)$$

Where:

E = either the adiabatic or polytropic compression efficiency, percent
k = the ratio of specific heats, C_p/C_v

$$T_d = T_s * R^\sigma \quad (6-8)$$

Where:

T_d and T_s = the absolute discharge and suction temperatures

Based on the test runs, there does not appear to be any indication of internal leakage since the calculated efficiencies from the suction and discharge temperatures appear to be essentially the same as the design. Thus, hypothesis 3 was eliminated.

As indicated earlier, one hypothesis was that the poor insulation was allowing a 10°F increase in temperature between the economizer and the blower suction. This increased suction temperature would cause an increase in polytropic head. To determine if this was a theoretically sound working hypothesis, the problem solver calculated the blower head assuming that the gas temperature stayed at -40°F. He got the results shown in Table 13-9.

If the gas temperature stayed at -40°F, the required head would have been reduced slightly. The reduced head would decrease the horsepower requirements. However, the system does not appear to be limited by power

requirements. As indicated in Table 13-6, the steam turbine driving the compressor remained at the design speed of 10000 rpm throughout the tests. Thus, it appeared that the probability that this hypothesis was correct seemed very low.

Step 4: Provide a Mechanism to Test the Hypothesis

The elimination of these hypotheses left only the alternative hypothesis that there was excessive leakage across the kickback valve. If leakage was occurring through this valve when it was in the closed position, that would explain both the increase in temperature between the economizer and the blower suction, as well as the poor performance of the blower relative to the manufacturer's supplied curve. Rather than immediately recommending a shut-down to inspect the valve, the problem solver decided to test the hypothesis with calculations. He reviewed the specifications for the 14-inch kickback valve. When he reviewed the specifications, he found that the valve was not specified as a "tight shutoff valve". In addition, a review of the drawings indicated that the butterfly valve had a peripheral clearance of 0.05 inches. That is, there was a clearance of 0.05 inches between the flap of the butterfly valve and the wall of the valve. He then estimated the leakage that could occur across the valve when it was completely closed. The flow rate through this small opening will be at sonic velocity. These calculations are as follows:

$$A = \pi * (D_1^2 - D_2^2) / 4 = \pi * (14^2 - 13.9^2) = 2.19 \text{ inches}^2 = 0.0152 \text{ feet}^2 \quad (13-8)$$

$$P = 0.55 * (14.7 + 10) = 13.58 \text{ psia} \quad (13-9)$$

$$VS = (P * g * k / \rho)^{0.5} = (13.58 * 144 * 32.2 * 1.25 / 0.065)^{0.5} = 1100 \text{ feet/second} \quad (13-10)$$

$$F = \rho * VS * A = 0.065 * 0.0152 * 1100 * 3600 = 3910 \text{ pounds/hr} \quad (13-11)$$

$$ES = F / (60 * \rho) = 3910 / (60 * 0.065) = 1000 \text{ ft}^3/\text{minute} \quad (13-12)$$

Where:

A = peripheral area with a clearance of 0.05 inches

D₁ = approximate diameter of valve, inches

D₂ = approximate diameter of the butterfly wafer, inches

P = pressure at restriction, psia

VS = sonic flow velocity, fps

g = gravity factor, fps²

k = specific heat ratio

ρ = gas density, lbs/ft³

F = flow rate through peripheral area, lbs/hr

ES = approximate volumetric flow, ft³/minute

A brief explanation of the sonic flow conditions modeled by equations (13-9) through (13-11) may be appropriate. Essentially all chemical engineering textbooks discuss this phenomenon in more detail than is possible in this book. The velocity across the peripheral opening will be at sonic flow velocity. This is because the pressure after the valve is only about 40 percent of the pressure before the valve. For a gas with a specific heat ratio (k) of 1.25, sonic flow properties occur if the pressure after a restriction is less than 55 percent of the pressure before the restriction. If sonic flow conditions are encountered, the maximum flow rate (sonic velocity) that will occur across any size opening with any amount of pressure drop is that which occurs when the outlet pressure is 55 percent of the inlet pressure. Thus, the actual flow rate across the peripheral opening is evaluated at 55 percent of the absolute inlet pressure (equation (13-9)) and at the sonic velocity and density at these conditions (equations (13-10) and (13-11)).

As shown above, the estimated leakage through the butterfly valve could account for a capacity loss of approximately 1000 ft³/minute. Referring to Figure 13-6, this difference in suction flow rate could explain the deficiency in performance of the blower.

Step 5: Recommend Remedial Action to Eliminate the Problem without Creating Another Problem

The problem solver was faced with no other reasonable recommendation to make except to shut down the system and replace the kickback valve with one that had a “tight shutoff” rating. The potential problems that had to be considered were:

- Was the replacement valve really a tight shutoff valve? Would it be possible to find a 14-inch valve that would fit into the space available and not have a peripheral opening similar to the existing valve?
- Would the new valve fit without making significant piping modifications? Could it be installed with a minimal amount of effort?
- Was there anything else that should be considered prior to a recommended shutdown? For example, should the efficiency of the steam turbine be determined to insure that it is performing as designed?

13.8 LESSONS LEARNED

This example problem indicates the value of doing a thorough problem analysis rather than just jumping to a conclusion that the blower is not performing as it was designed. If a complete analysis had not been done, the blower might have been shut down for an inspection or additional insulation might have been added to the blower suction lines in hopes that this would improve the

performance. Either of these solutions that on the surface seemed to make sense would have delayed finding the fact that the “kickback” valve was leaking. If the blower had been shut down for an inspection and/or replacement of wear rings without knowledge that the kickback valve was leaking, another shutdown would have been required to replace the kickback valve. The analysis done illustrates the value of doing calculations to prove or disprove hypotheses.

As indicated in Chapter 3, a component of successful plant problem solving is a daily monitoring system that allows for the early detection of problems. This early detection will provide an earlier initiation of problem-solving activities than if the problem is allowed to continue to develop. If such a system had been in place in this example, a plot of “head curve deviation” as defined in Table 13-6 would have likely provided an early signal that there was a performance deficiency. An even better approach for a critical piece of revised equipment is to conduct a performance test as soon after start-up as possible.

The problem with the leaking “kickback” valve could have been detected even earlier than the start-up of the expanded facilities. If a plant test had been run prior to the shutdown to expand the plant or if the blower performance had been monitored on a daily basis, the problem with the valve could have been detected prior to the expansion. This would have eliminated the downtime required to replace the valve after the facilities start-up.

A conservative approach of inspecting the blower during the shutdown to replace the kickback valve could have been taken. However, this would have required major mechanical work and extended the time of the shutdown. Since the calculated polytropic efficiency was very close to the design value of 70 percent, it is highly unlikely that this would have been a “value-added” exercise.

13.9 EXAMPLE PROBLEM 13-4: THE VALUE OF A POTENTIAL PROBLEM ANALYSIS

While the utilization of a potential problem analysis was not emphasized in the previous problems, it would have been of great value for Example Problem 13-4.

A new fractionation process was designed to minimize cost by eliminating a reboiler, minimizing instrumentation and maximizing heat integration. The fractionation tower products were a high purity overhead and a high purity bottoms stream.

A simplified sketch of the process is shown in Figure 13-7.

As shown in Figure 13-7, the feed to the tower is fractionated into a high purity overhead methanol product and a high purity xylene bottoms product. The heat integration is such that the heat input to the tower consists of a controlled vapor flow of xylene from a furnace. This vapor is the same material

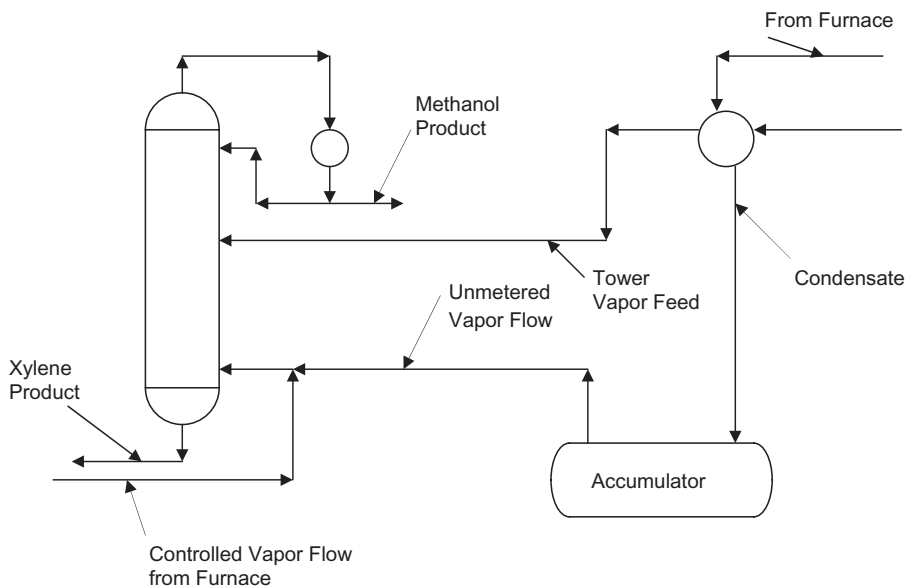


Figure 13-7 Simplified sketch of fractionation system.

as the high purity bottoms product so that no reboiler is required. That is, the vapors from the furnace are fed directly to the tower to provide heat input. The tower reflux is controlled to maintain a tower temperature profile. In addition to the controlled vapor flow to the bottom of the tower, the vapor output from the furnace is also used to heat the tower feed in exchangers. The xylene vapors condensed in the exchangers then flow to the accumulator as shown in Figure 13-7. The design of the exchangers was such that at *full capacity* and at the *design heat transfer coefficient* of the exchanger, the outlet material from the exchanger would be condensed xylene at the boiling point and pressure of the accumulator. That is, there would be no significant vapor flow from the accumulator to the tower. The fact that there was no meter on this flow back to the tower did not seem like a significant problem since there would normally be no flow in the line. However, the designer recognized that there might be times when the conditions were such that the material leaving the exchanger would not be totally condensed and might contain vapor flowing into the accumulator, he provided a vent line to allow uncondensed vapors from the accumulator to flow to the tower. The designer believed that in cases where the vapor did vent out of the accumulator in an uncontrolled fashion, the control system would “take care of things” by adding more reflux to the tower.

As often happens, processes that are designed for steady state are rarely operated at steady state. The heat content of the material flowing into the accumulator was constantly changing. At times, there would be two phases (vapor and liquid) entering the drum. In this case, vapor would vent out of

the drum into the tower. At other times, the xylene being condensed in the exchanger would be cooled to the point that the material entering the accumulator would be below the boiling point at accumulator pressure. If this occurred, vapor would flow back out of the tower. The predominant situation was the unsteady-state cycling of no vapor being vented back to the tower, transitioning to one where there were two phases in the flow to the accumulator. In this case, when there were two phases present in the flow to the accumulator, vapor would flow uncontrollably to the tower creating an increase in the heat flow to the tower. The control system would respond *after* the temperature profile was disturbed and would cause more reflux to be added to the tower. During this transient condition, the purity of the overhead product stream would be less than desired since the increased vapor rate would cause more low volatility material to be carried overhead until the control system responded and increased the reflux rate. If the reflux rate had to be increased too much to compensate for the vapor venting out of the accumulator, it was possible that the tower would flood. As this situation transitioned to one where there was no vapor vent from the accumulator, the temperature profile in the tower would again be upset since there was now excessive reflux going to the tower. Again the control system would correct the reflux rate, but only after the bottoms product was off specification.

When the converse situation occurred, the vapor flowed back out of the tower due to the low pressure in the accumulator. In this case, the temperature profile would again be disturbed and the control system would again respond *after* the disturbance occurred. In this case, it was generally the bottoms stream that would be below specification during the transient.

The problem solver used the five-step procedure discussed earlier to begin solving the problem.

Step 1: Verify that the Problem Actually Occurred

The initial description of the problem was only that something was causing an upset in the tower and the operations people believed that it was somehow associated with the accumulator. They often tried to compensate for these upsets by trying to adjust the controlled vapor rate. However, this was largely “guesswork” and often made things worse. The problem solver verified that upsets in the tower were being caused by changes (increases or decreases) in the fraction of vapor in the condensate flowing to the accumulator.

Step 2: Write Out an Accurate Statement of What Problem You Are Trying to Solve

The problem solver wrote out the following problem description:

“Fractionation tower upsets are being caused by changes in an unmetered flow going to the bottom of the tower. These changes in the unmetered flow cause

an increase or decrease in heat input to the bottom of the tower, the temperature profile in the tower to be upset, and the purity of the distillate and bottom products to be off specification. Determine how to eliminate the fractionation tower upsets caused by changes in an unmetered flow going to the bottom of the tower.”

Step 3: Develop a *Theoretically Sound Working Hypothesis* that Explains the Problem

In this example, a start of the working hypothesis that explains the problem was included as part of the problem statement. However, it was not obvious how to solve the problem until the hypothesis was more fully developed. The questions given in Chapter 5 were used to fully develop a working hypothesis for obtaining a solution to the problem as shown in Table 13-10.

The only two reasonable hypotheses were that the assumption of steady-state operations was not valid and the possibility that a construction error had been made. No specific hypothesis was developed that would tie construction errors to the symptoms being observed. While it was possible that an error in the tray design, fabrication or installation might be possible for fractionation upsets at the extreme conditions of high rates of uncontrolled vapors to the tower, it seemed unlikely that these tray errors would not show up at other times. Exploring the construction error hypothesis would likely require elaborate test equipment and/or a tower shutdown. It was decided to first consider the possibility that the original assumption of steady-state operation was the primary cause of the problem. It was clear that if the temperature of the condensate returning to the drum was not at the boiling point at the pressure in the drum that there would be an unmetered flow either to or from the tower. Developing the simplest solution that will work the problem as pointed out in Chapter 3 is always the best approach.

Thus, the problem solver developed the following hypothesis:

“It is believed that the problems associated with the control of the tower are due to the fact that the heat content of the stream leaving the exchangers is not constant. At times there are large amounts of vapor in this stream which then vent to the tower as an uncontrolled heat input. At other times the stream leaving the exchangers is subcooled which causes vapors to flow from the tower to the accumulator. Tower control will be greatly improved if the vent or backflow from the accumulator can be measured.”

Step 4: Provide a Mechanism to Test the Hypothesis

As what was thought to be a permanent solution to the problem, a venturi meter was installed in the vapor line. The venturi meter was selected because it would have a low-pressure drop and because it had the inherent capability

Table 13-10 Questions/comments for Problem 13-4

Question	Comment
Are all operating directives and procedures being followed?	All operating directives and procedures were being followed. New ones were considered, but would not solve the problem.
Are all instruments correct?	Yes.
Are laboratory results correct?	Not applicable in this case.
Were there any errors made in the original design?	The assumption of steady state was not valid.
Were there changes in operating conditions?	No.
Is fluid leakage occurring?	Not applicable.
Has there been mechanical wear that would explain the problem?	No.
Is the reaction rate as anticipated?	Not applicable.
Are there adverse reactions occurring?	Not applicable.
Were there errors made in the construction of the process?	Since the unit had only recently been built, this had to be considered.

to measure flow in both directions. If the enthalpy of the flow to the accumulator was such that some flashing occurred in the accumulator, the venturi would measure flow from the accumulator into the tower and the controlled vapor rate from the furnace would be reduced to compensate for this vapor flow from the accumulator. Thus, the vapor rate in the tower would remain constant. Conversely, if the enthalpy of the flow into the accumulator was such that the liquid in the accumulator was subcooled creating backflow from the tower, the controlled vapor rate would be increased to compensate for this backflow. It was believed that the installation of the venturi meter would maintain the vapor flow in the tower constant and thus avoid tower upsets. The control algorithm for the system is described as shown below:

$$F = V - Y + ZF \quad (13-13)$$

Where:

V = the tower internal vapor rate which should be held constant

F = the controlled vapor rate from the furnace

Y = the flow rate from the accumulator to the tower

ZF = the flow rate from the tower to the accumulator

A simplified sketch of the venturi meter design is shown in Figure 13-8. A typical venturi pressure profile is also shown for the case where there is flow from the accumulator to the tower. It was recognized that the accuracy of the

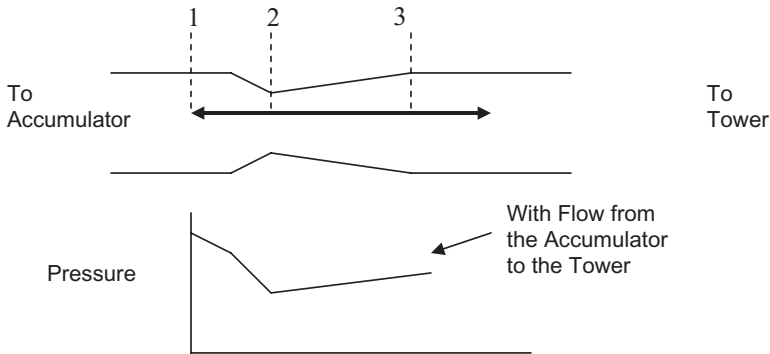


Figure 13-8 Venturi sketch.

flow from the accumulator to the tower (measured by the pressure drop from point 1 to 2) would be more accurate than the backflow from the tower to the accumulator (measured by the pressure drop from point 3 to 2).

Unfortunately, no potential problem analysis as suggested in Chapter 3 for this problem solution was done. The fact that there is pressure recovery with any type of meter was not considered. This pressure recovery is represented in the sketch as the pressure increases from point 2 to point 3 when flow is from the accumulator to the tower. Since the pressure at point 3 is greater than the pressure at point 2, the control system would assume that this was backflow from the tower. The control system would then have values for both “Y” and “ZF”. Of course when flow was from the accumulator to the tower, the actual value of “ZF” was zero. However, the pressure recovery made the control system think that “ZF” had a nonzero value. A potential problem analysis that included a detailed understanding of the venturi meter would have discovered this problem and allowed an engineering solution well before start-up of the revised facilities.

Step 5: Recommend Remedial Action to Eliminate the Problem without Creating Another Problem

After the initial start-up difficulties discussed above, a selector switch was installed to allow the control scheme to select the greater value of “Y” or “ZF” and set the other variable to zero. The system performed flawlessly after that minor modification.

13.10 LESSONS LEARNED

There are several lessons that can be learned from this problem. While the skill of process design involves the assumption of steady state, consideration

should always be given to the question of “How does unsteady state impact the design?” If the process designer had considered unsteady state, it is likely that he would have provided flow-measuring devices as part of the original design. The problem solver can also use the question of “How does unsteady state impact things?” as a problem-solving tool by questioning the validity of the steady-state assumption.

There is great value in both understanding the equipment involved in a problem solution and in performing a potential problem analysis prior to making a recommendation. In the example given here, the fact that pressure recovery would impact the results was blatantly obvious to anyone with a minimal knowledge of flow instruments. However, in the rush to get the facilities designed and installed, it was overlooked. A potential problem analysis would have pinpointed this problem before the venturi meter was installed. Potential problem analyses are often not done except if they are required as part of a disciplined procedure.

Chapter 13 Table of nomenclature

- A Area. In this chapter, it is used to represent the area of a restriction or a peripheral area with a clearance of 0.05 inches. The value is in ft^2
- C A constant referred to as the “lumped parameter constant”
- D_1 The approximate diameter of valve, inches
- D_2 The approximate diameter of the butterfly wafer, inches
- DF The driving force or incentive for reaction to occur, mols of chlorine derivative gas absorbed/ ft^3 of TEG
- E Either the adiabatic or polytropic compression efficiency, percent
- ES The approximate volumetric flow, $\text{ft}^3/\text{minute}$
- F Flow rate. In this chapter, it is used to represent the ion-exchange bed feed rate, flow rate through a peripheral area, the flow of steam through the restriction, or the controlled vapor rate from the furnace all in lbs/hr
- g Gravity factor, fps^2
- H The polytropic or adiabatic head, feet
- k The ratio of specific heats, C_p/C_v
- M The gas molecular weight
- P The pressure at restriction, psia
- R The compression ratio
- R^* The rate of change with time per unit volume of the compound under study, mols of $\text{HCl}/\text{ft}^3\text{-minute}$ that are formed
- RC The rate of chloride production in the United States, lbs/hr
- S The density of the flowing fluid relative to water

T_D	The absolute discharge temperature
T_S	The suction temperature, °R
U	The velocity of the flowing fluid through the orifice, fps
V	The tower internal vapor rate which should be held constant
VS	The sonic flow velocity, fps
X_F	The concentration of chlorides in the flow to the ion-exchange bed, weight fraction
Y	The flow rate from the accumulator to the tower
Z	The average (suction and discharge) compressibility
Z_F	The flow rate from the tower to the accumulator
ΔP	The pressure drop across the restriction, psi
ρ	The fluid density, lbs/ft ³
σ	The polytropic or adiabatic compression exponent

A FINAL NOTE

Since problem solving as described in this book is not an intuitive process, there will be a learning period or an induction period before it can be done efficiently. This learning period will result in the first few problems or first few calculations that are done using this process being slow and labor intensive. My personal assessment is that the first time that a new calculation technique is utilized that it often takes 5 to 10 times as long to do the calculation as after the calculation technique becomes “second nature”. This is because the problem solver often will not have a feel for what the magnitude of the value that he is calculating should be, and he will conservatively check his calculations against some known standard. However, as experience is gained with this technique, speed will increase and some of the labor-intensive steps will become almost automatic. Best of all, problems will be solved one time for all time. In addition, as indicated in earlier chapters, this approach is not to be used for every plant problem-solving activity. There will always be questions of “optimum technical depth” to consider.

There are some guidelines that should be considered prior to beginning to either implement these techniques as an individual or as a manager to implement these techniques throughout an organization. Some of these guidelines have been mentioned in earlier chapters. The purpose of this chapter is to present some of these guidelines together in one location.

The problem solver and his management should realize that the first time these techniques are used that more time will be required. The process of using a list of questions, such as those in Chapter 5, to develop a working hypothesis

will be cumbersome until it is done a few times. There will be calculation techniques that the problem solver is not familiar with. He may well want to check his calculations because he has not yet developed an intuitive feel for the particular calculation. Management can be of great assistance in this area by insisting that they want the problem solver to take the time to do it right and insist on using the techniques described in this book. Our culture demands quick answers in almost all areas. From video games to interactive computer-aided learning, we have become an iterative society. The high school student that is using the computer to study often can keep trying to get the answer without any thought or calculation until he “gets it right”. It will take strong management action to insist on replacing this “quick answer culture” with a “do it right culture”.

The problem solver should recognize the role that the operator or mechanic can play in problem solving. The data that they have is invaluable in developing a theoretically sound working hypothesis. They have first-hand experiences and have made observations that are not available via any other means such as process control computers, instrumentation or laboratory results. They may at times have problems putting their observations or experiences into quantitative descriptions. The problem solver can help them express themselves by patiently asking questions. However, regardless of how much experience and valuable input they may have, they may not have sufficient training to formulate a correct working hypothesis. Their input and relationships should be cultivated by the professional.

There will be times when it is necessary to make assumptions. Many times in industrial problem solving, the direction of the change and the order of magnitude of the impact is all that is required. An exact value may not be required. For example, it may be necessary to assume the constant in the relationship between the rate and the driving force. The problem solver should not be discouraged by the need to make an assumption. It is often more important to get the form of the driving force correct than it is to get the constant correct. As described in Example Problem 13-1 given in Section 13.3, knowing the relationship between chloride production and residence time was much more important than the actual rate constant.

Bureaucracy should be avoided at all costs. There will be a tendency for management to micromanage the exact wording of the document described in Table 3-3. This problem specification is meant to be used by the problem solver to provide the best description possible of the problem that he is trying to solve. Wording changes will no doubt end up diluting and confusing his efforts. On the other hand, a review of the final conclusions and proposals to conduct tests to prove the hypothesis is mandatory. These reviews should focus on the technical accuracy of the calculations and the preparation for any proposed plant tests. Safety should be a major component of this review.

The concept of “one riot, one ranger” as described in Section 5.6 should be utilized. While committees are of value, management should make it absolutely clear who has responsibility for developing a problem solution.

There may be value in initially having an individual assigned as the sponsor for utilization of these problem-solving procedures. This individual would be available to consult in the utilization of each of the procedural steps. He would not necessarily be an expert in the process of interest or in the utilization of equipment calculations. However, he would have sufficient know-how in the techniques to insure that all the steps in the process were adequately considered.

APPENDIX 1 LITERATURE REFERENCES

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Hydrocarbon Processing, September 1968, Volume 47, Number 9, page 253

Reciprocating Pumps by Terry L. Henshaw

Chemical Engineering, September 21, 1981, page 105

APPENDIX 2 CONVERSION FACTORS FROM ENGLISH UNITS TO CGS UNITS

English Units	CGS Units	Multiply by to Go to CGS
Feet (f)	Meter (m)	0.3048
Pounds (lbs)	Kilograms (kg)	0.454
Pounds/inch ² (psi)	Bar (bar)	0.069
Gallons (g)	Liters (L)	3.785
BTU	Calories (cal)	252
Centipoise (cP)	Poise (P)	0.01
Horsepower (BHP)	Kilowatt (kw)	0.746
Degrees Fahrenheit (°F)	Degrees Centigrade (°C)	(°F - 32)*0.5556
Degrees Rankin (°R)	Degrees Kelvin (°K)	0.5556

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5ª edición

Química Orgánica



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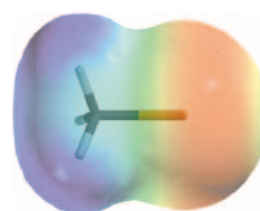
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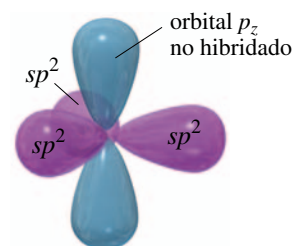


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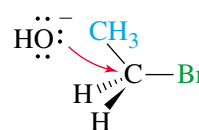
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bromuro de etilo (1°)
el ataque es fácil



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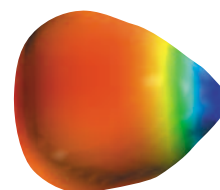
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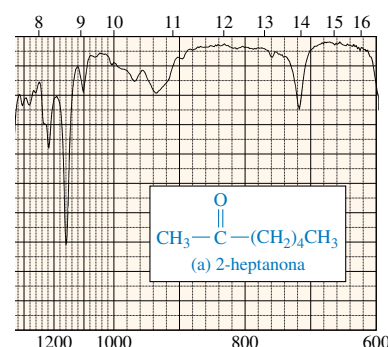
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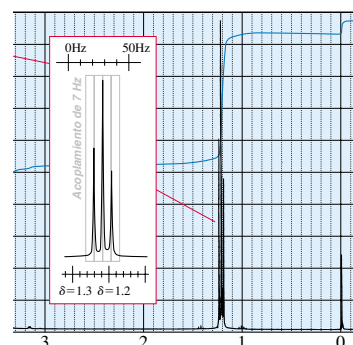


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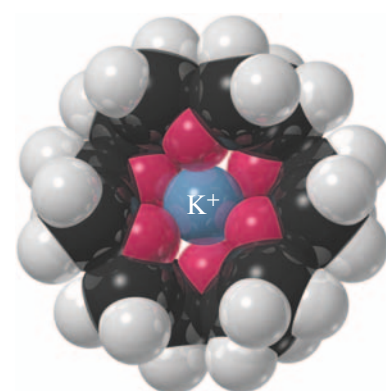
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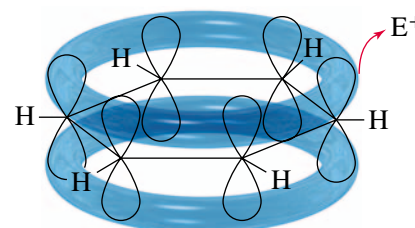
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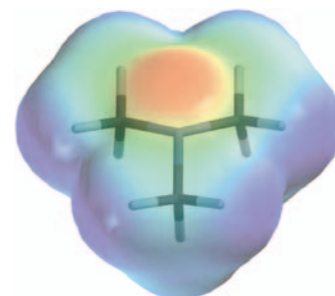
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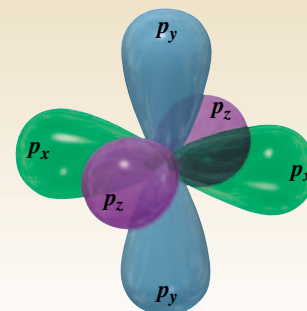
Soluciones de los problemas seleccionados A1

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CAPÍTULO 1

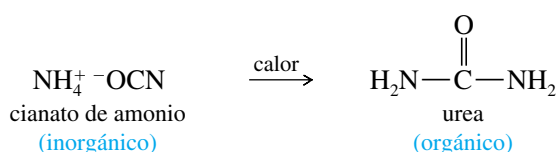
Introducción y revisión



La definición moderna de **química orgánica** es la *química de los compuestos de carbono*. ¿Qué tiene de especial el carbono que hay una rama de la química que se dedica a él? Al contrario que otros elementos, el carbono forma enlaces fuertes con otros átomos de carbono y con una gran variedad de otros elementos. Las cadenas y anillos de átomos de carbono son tan variadas que se puede formar una variedad interminable de moléculas. Esta diversidad de los compuestos de carbono es la base para la vida en la Tierra. Los seres vivos están formados de compuestos orgánicos complejos con funciones estructurales, químicas o genéticas.

El término **orgánico** literalmente significa «derivado de los organismos vivos». Originalmente, la ciencia de la química orgánica era el estudio de los compuestos que se extraían de los organismos vivos o productos naturales. Compuestos tales como azúcar, urea, levadura, ceras y aceites vegetales eran considerados «orgánicos» y se aceptó el **Vitalismo** como teoría que explicaba su origen: la creencia en que los productos naturales necesitaban una «fuerza vital» para ser creados. Por tanto, la química orgánica era el estudio de los compuestos que tenían esa fuerza vital. La química inorgánica era el estudio de los gases, rocas, minerales y de los compuestos que se podían obtener a partir de ellos.

En el siglo XIX, la experimentación demostró que los compuestos orgánicos se podían sintetizar a partir de compuestos inorgánicos. En 1828, el químico alemán Friedrich Wöhler convirtió el cianato de amonio, obtenido a partir de amoníaco y ácido ciánico, en urea simplemente calentando el cianato en ausencia de oxígeno.



La urea también proviene de los seres vivos y se creía que contenía la fuerza vital, a pesar de que el cianato de amonio es inorgánico y por tanto, según aquella creencia, no poseía la fuerza vital. Algunos químicos sostenían que esa fuerza vital provenía de las manos de Wöhler, pero la mayoría reconocieron la posibilidad de sintetizar compuestos orgánicos a partir de compuestos inorgánicos. También se llevaron a cabo otras síntesis, por lo que la teoría de la fuerza vital se descartó.

Desde que el Vitalismo se descartó a comienzos del siglo XIX, se podría pensar que esta idea habría ya desaparecido, pero estaríamos equivocados, ya que el Vitalismo hoy forma parte de la mentalidad de las personas que creen que los productos «naturales» (derivados de las plantas) son diferentes y más saludables que aquellos compuestos exactamente iguales, «artificiales», que han sido sintetizados.

Como químicos, sabemos que los compuestos derivados de las plantas y los compuestos sintetizados son idénticos. La única diferencia es el contenido en ^{14}C : los compuestos sintetizados a partir de derivados del petróleo tienen menor contenido del isótopo radioactivo ^{14}C ,

1.1

Los orígenes de la química orgánica



El corazón artificial Jarvik 7 está compuesto en gran parte de materiales orgánicos sintéticos.

ya que este isótopo ha ido desapareciendo con el tiempo. Los compuestos derivados de las plantas, al haber sido sintetizados recientemente a partir del CO_2 del aire, tienen un contenido más elevado en ^{14}C . Algunos suministradores importantes de productos químicos dan los análisis de los isótopos para confirmar que los «productos naturales» que distribuyen tienen mayor contenido en ^{14}C y son derivados de las plantas. Estos sofisticados análisis dan un aspecto de alta tecnología al Vitalismo del siglo XXI.

A pesar de que los compuestos orgánicos no necesitan una fuerza vital, todavía se diferencian de los compuestos inorgánicos. La característica que distingue a los compuestos orgánicos es que *todos* contienen uno o más átomos de carbono. Pero no todos los compuestos que contienen carbono son orgánicos, sustancias tales como: diamante, grafito, dióxido de carbono, cianato de amonio y carbonato de sodio son compuestos derivados de minerales, y tienen propiedades características de los compuestos inorgánicos. No obstante, la mayoría de los millones de compuestos que contienen carbono se clasifican como orgánicos.

Nosotros mismos estamos compuestos en gran parte por moléculas orgánicas y nos alimentamos de compuestos orgánicos. Las proteínas de nuestra piel, los lípidos de las membranas de nuestras células, el glucógeno de nuestro hígado y el DNA del núcleo de nuestras células son compuestos orgánicos. Nuestros cuerpos también están regulados y son defendidos por compuestos orgánicos complejos.

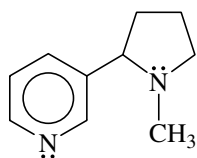
Los químicos han aprendido a diseñar y sintetizar muchas de estas moléculas complejas. Los productos sintéticos se utilizan como productos farmacéuticos, plásticos, pesticidas, pinturas y fibras. La mayoría de los avances más importantes en medicina se debe actualmente a los avances en química orgánica. Así, se sintetizan nuevos productos farmacéuticos para combatir enfermedades y se obtienen nuevos polímeros para elaborar dispositivos ortopédicos con los que sustituir órganos dañados. La química orgánica ha cerrado el ciclo, comenzó con el estudio de los compuestos derivados de «órganos» y ahora nos proporciona los productos farmacéuticos y materiales que necesitamos para salvar o reemplazar esos órganos.

Uno de los efectos de la nicotina es incrementar la concentración de una sustancia química en el sistema de estímulos cerebrales. La liberación de esta sustancia química hace que los fumadores se sientan bien y refuerza la necesidad de fumar.

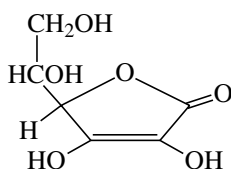
Una de las razones por las que los químicos sintetizan derivados de compuestos orgánicos complejos como la morfina es descubrir nuevas sustancias que mantengan sus propiedades útiles (analgésia) pero no las propiedades indeseables (adicción).



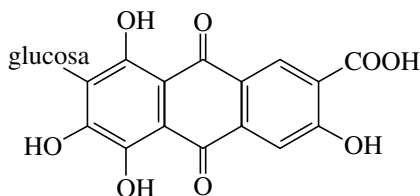
nicotina



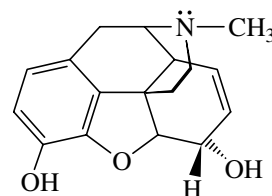
vitamina C



carmín



morfina



A continuación daré cuatro ejemplos de compuestos orgánicos aislados de organismos vivos: el tabaco contiene nicotina, un alcaloide que crea adicción; los escaramujos contienen vitamina C, esencial para prevenir el escorbuto; el carmín proviene de las cochinillas, insectos que suelen estar en las chumberas, y las adormideras contienen morfina, sustancia que mitiga el dolor pero provoca adicción.

Antes de comenzar el estudio de la química orgánica, se han de revisar algunos principios básicos. Muchos de los conceptos de estructura atómica y molecular son cruciales para entender la estructura y el enlace de los compuestos orgánicos.

1.2A Estructura del átomo

Los átomos están formados por protones, neutrones y electrones. Los protones están cargados positivamente y se encuentran, junto con los neutrones (sin carga), en el núcleo. Los electrones contienen una carga negativa de la misma magnitud que la carga positiva de los protones y se encuentran en el espacio que rodea al núcleo (Figura 1.1). Los protones y los neutrones tienen una masa parecida, aproximadamente unas 1800 veces la masa de un electrón. A pesar de que prácticamente toda la masa del átomo está concentrada en el núcleo, son los electrones los que participan en los enlaces químicos y en las reacciones.

Cada elemento se caracteriza por el número de protones que tiene en el núcleo (número atómico). El número de neutrones normalmente es parecido al número de protones, pero este número de neutrones puede variar. Los átomos que tienen el mismo número de protones pero diferente número de neutrones se llaman **isótopos**. Por ejemplo, el átomo de carbono más común es el que tiene seis protones y seis neutrones en el núcleo; su número másico (suma de protones y de neutrones) es 12, por lo que lo escribimos con el símbolo ^{12}C . Aproximadamente el 1% de los átomos de carbono tienen 7 neutrones y su número másico es 13, simbolizado por ^{13}C . Una fracción muy pequeña de átomos de carbono tiene ocho neutrones, por lo que su número másico es 14. El ^{14}C es un isótopo radioactivo, con un periodo de semidesintegración (tiempo que tarda una determinada masa de ese isótopo en desintegrarse y perder la mitad de su masa) de 5 730 años. Este tiempo de desintegración del ^{14}C se utiliza para determinar la edad de los materiales orgánicos de hasta unos 50 000 años de antigüedad.

1.2B Estructura electrónica del átomo

Las propiedades químicas de un elemento se determinan por el número de protones de su núcleo y el correspondiente número de electrones que hay alrededor del núcleo. Los electrones forman enlaces y determinan la estructura de las moléculas resultantes. Debido a que los electrones son muy pequeños y están en movimiento, se comportan simultáneamente como partículas y como ondas.

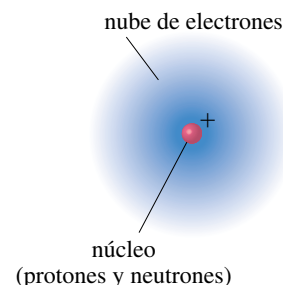
Los electrones que se encuentran moviéndose alrededor del núcleo se encuentran en **orbitales**. El principio de incertidumbre de Heisenberg dice que nunca se puede determinar con exactitud dónde se encuentra el electrón; sin embargo, se puede determinar la **densidad electrónica**, la probabilidad de encontrar al electrón en una determinada zona del orbital. Por tanto, un orbital es un estado de energía permitido para un electrón, con una función de probabilidad asociada que define la distribución de la densidad electrónica en el espacio.

Los orbitales atómicos se agrupan en «capas» o niveles diferentes a distintas distancias del núcleo. Cada capa se identifica por un número cuántico principal n , siendo $n = 1$ para la capa de menor energía (la que está más próxima al núcleo). Al aumentar n , las capas están más alejadas del núcleo, tienen una energía más alta y pueden contener más electrones. La mayoría de los elementos más comunes de los compuestos orgánicos se encuentran en las dos primeras filas (periodos) de la tabla periódica, lo que indica que sus electrones se encuentran en las dos primeras capas de electrones. La primera capa ($n = 1$) puede alojar dos electrones y la segunda capa ($n = 2$) puede alojar ocho.

La primera capa de electrones contiene solamente el orbital $1s$. Todos los orbitales s tienen simetría esférica, lo cual quiere decir que son no direccionales. La densidad electrónica del orbital $1s$ se representa en la Figura 1.2. Se puede observar que la densidad electrónica es más alta en las proximidades del núcleo y va disminuyendo exponencialmente según va aumentando la distancia al núcleo. Se podría comparar el orbital $1s$ con una cápsula de algodón, donde la semilla representaría el núcleo. La densidad del algodón es mayor en los lugares próximos a la semilla y su densidad va disminuyendo según se va alejando del núcleo.

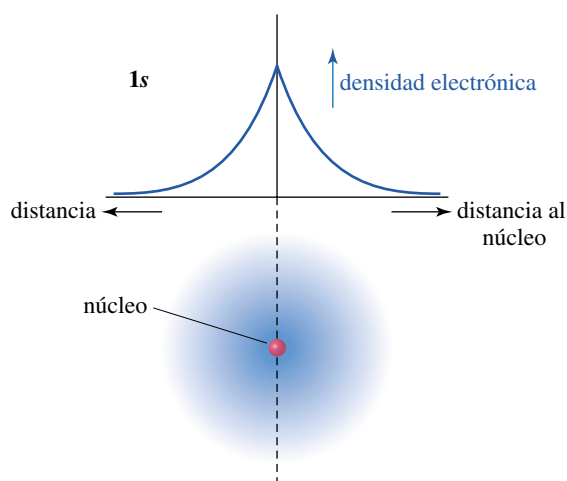
La segunda capa de electrones consta de orbitales $2s$ y $2p$. El orbital $2s$ posee simetría esférica igual que el $1s$, pero su densidad electrónica no es una simple función exponencial. El orbital $2s$ tiene una densidad electrónica más pequeña en las proximidades del

1.2 Principios de la estructura atómica



▲ Figura 1.1

El átomo tiene un denso núcleo, cargado positivamente, rodeado de una nube de electrones.

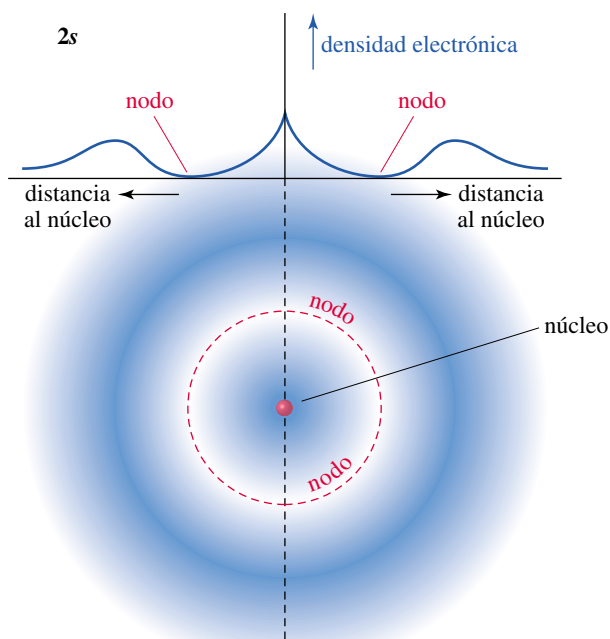


► Figura 1.2

Gráfico y diagrama del orbital atómico 1s. La densidad electrónica es más alta cerca del núcleo y disminuye exponencialmente al aumentar la distancia al núcleo en cualquier dirección.

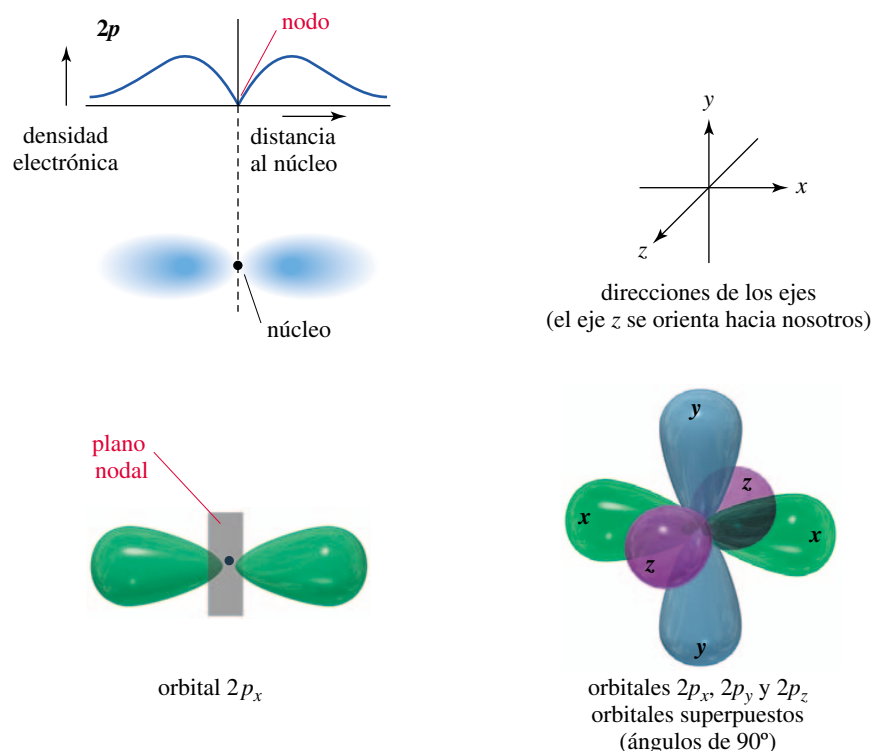
núcleo, ya que la mayor parte de la densidad electrónica está más alejada, más allá de una zona de densidad electrónica nula llamada **nodo**. Como la densidad electrónica del orbital 2s cerca del núcleo es menor que en el caso del orbital 1s, el orbital 2s tiene energía más alta. La Figura 1.3 muestra una representación gráfica del orbital 2s.

Además del orbital 2s, la segunda capa también contiene tres orbitales atómicos 2p, orientados cada uno de ellos en las tres direcciones del espacio. Estos tres orbitales reciben el nombre $2p_x$, $2p_y$ y $2p_z$, según su orientación a lo largo de los ejes x , y o z . Los orbitales 2p tienen una energía ligeramente superior a la de los orbitales 2s, debido a que la localización media de los electrones en los orbitales 2p se sitúa a una distancia más alejada del núcleo. Cada orbital p consta de dos lóbulos, uno a cada lado del núcleo, con un **plano nodal** en el núcleo. El plano nodal es una región (plana) del espacio que incluye el núcleo y tiene una densidad electrónica nula. Los tres orbitales 2p únicamente difieren en sus orientaciones espaciales, por lo que tienen la misma energía. Los orbitales que tienen la misma cantidad de energía reciben el nombre de **orbitales degenerados**. La Figura 1.4 muestra las formas de los tres orbitales atómicos 2p degenerados.



► Figura 1.3

Los orbitales 2s tienen una pequeña región de densidad electrónica elevada próxima al núcleo, pero la mayor parte de la densidad electrónica está alejada del núcleo, más allá del nodo o región de densidad electrónica cero.



◀ **Figura 1.4**

Orbitales $2p$. Hay tres orbitales $2p$, orientados unos con respecto a los otros perpendicularmente. Se nombran según su orientación a lo largo del eje x , y o z .

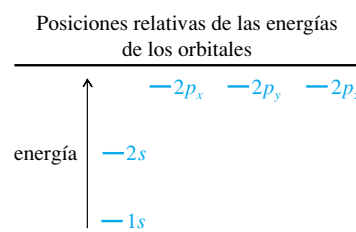
El *principio de exclusión de Pauli* dice que un orbital como máximo puede alojar dos electrones, de forma que sus espines estén apareados. La primera capa (un orbital $1s$) puede alojar dos electrones. La segunda capa (un orbital $2s$ y tres orbitales $2p$) puede alojar ocho electrones y la tercera capa (un orbital $3s$, tres orbitales $3p$ y cinco orbitales $3d$) puede alojar 18 electrones.

1.2C Configuraciones electrónicas de los átomos

Aufbau significa «construir» en alemán, y el *principio de aufbau* explica cómo establecer la configuración electrónica de un átomo en su estado fundamental (el de mayor estabilidad). Se comienza con el orbital de energía más baja y se van llenando ordenadamente de menor a mayor energía hasta que se han colocado todos los electrones. La Tabla 1.1 muestra las configuraciones electrónicas en estado fundamental de todos los elementos que forman parte de los dos primeros periodos de la tabla periódica.

TABLA 1.1 Configuraciones electrónicas de los elementos del primer y segundo periodo

Elemento	Configuración	Electrones de valencia
H	$1s^1$	1
He	$1s^2$	2
Li	$1s^2 2s^1$	1
Be	$1s^2 2s^2$	2
B	$1s^2 2s^2 2p_x^1$	3
C	$1s^2 2s^2 2p_x^1 2p_y^1$	4
N	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	5
O	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	6
F	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$	7
Ne	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$	8



► **Figura 1.5**

Primeras tres filas de la tabla periódica. La organización de la tabla periódica se debe al alojamiento de los electrones en los orbitales por orden creciente de energía. Para estos elementos representativos, el número de la columna corresponde al número de electrones de valencia.

El carbonato de litio, una sal de litio, es un antidepresivo que se utiliza para tratar el problema psiquiátrico conocido como manía. La manía está caracterizada por comportamientos tales como alteraciones del humor, sentimientos de grandeza, obsesiones y dificultad para dormir. No se sabe cómo actúa el carbonato de litio cuando estabiliza el humor de este tipo de pacientes.

Detalle de la tabla periódica

IA							gases nobles (VIII)
H	IIA	IIIA	IVA	VA	VIA	VIIA	He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

En la Tabla 1.1 se ilustran dos conceptos adicionales. Los **electrones de valencia** son los electrones que se encuentran en la capa más externa. El carbono tiene cuatro electrones de valencia, el nitrógeno cinco y el oxígeno seis. El helio tiene dos electrones de valencia y el neón tiene ocho, lo que corresponde, respectivamente, a la primera capa de valencia y a la segunda capa de valencia llenas. En general (para los elementos representativos), la columna o número de grupo de la tabla periódica corresponde al número de electrones de valencia (Figura 1.5). El hidrógeno y el litio tienen un electrón de valencia y los dos se encuentran en la primera columna (grupo IA) de la tabla periódica. El carbono tiene cuatro electrones de valencia y está en el grupo IVA de la tabla periódica.

Observad en la Tabla 1.1 que los electrones de valencia tercero y cuarto del carbono no están apareados, ocupan orbitales separados. A pesar de que el principio de exclusión de Pauli dice que dos electrones pueden ocupar el mismo orbital, los electrones se repelen uno a otro, y el apareamiento requiere energía adicional. La **regla de Hund** afirma que cuando hay dos o más orbitales de la misma energía, los electrones preferentemente se alojan en orbitales *diferentes* antes que aparearse en un mismo orbital. El primer electrón $2p$ (caso del boro) se coloca en un orbital $2p$, el segundo (caso del carbono) en un orbital diferente y el tercero (caso del nitrógeno) se coloca en el último orbital $2p$. El cuarto, quinto y sexto electrón $2p$ se aparearán, respectivamente, con los tres primeros electrones.

PROBLEMA 1.1

Escriba las configuraciones electrónicas de los elementos de la tercera fila que se muestra en la tabla periódica parcial de la Figura 1.5

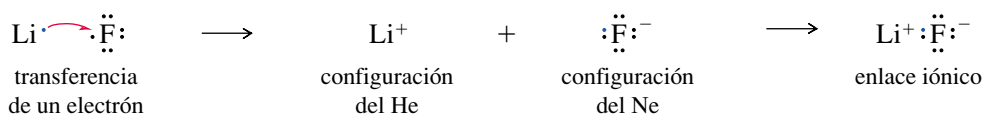
1.3

La formación del enlace: la regla del octeto

En 1915, G. N. Lewis propuso varias teorías nuevas para describir cómo se enlazaban los átomos unos a otros para formar moléculas. Una de esas teorías afirma que una capa llena de electrones es especialmente estable y que *los átomos transfieren o comparten electrones para que de esa forma las capas se llenen de electrones*. Una capa llena de electrones tiene la configuración de un gas noble como el He, Ne o Ar. A este principio se le dio el nombre de la **regla del octeto** porque una capa llena implica ocho electrones de valencia para los elementos de la segunda fila de la tabla periódica.

1.3A Enlace iónico

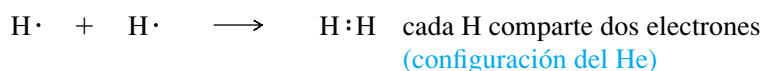
Hay dos formas en las que los átomos pueden interactuar para adquirir configuraciones de gas noble. Algunas veces los átomos adquieren configuraciones de gas noble transfiriendo electrones de un átomo a otro. Por ejemplo, el litio tiene un electrón más en su configuración que el helio, y el fluor tiene un electrón menos que la configuración del neón; el litio pierde fácilmente sus electrones de valencia y el fluor los gana fácilmente:



La transferencia de un electrón da a cada uno de los elementos la configuración de gas noble. Los iones resultantes tienen cargas opuestas y se atraen uno a otro formando un **enlace iónico**. El enlace iónico normalmente da lugar a la formación de grandes estructuras cristalinas en vez de moléculas individuales. El enlace iónico es muy frecuente en los compuestos inorgánicos, pero bastante inusual en los orgánicos.

1.3B Enlace covalente

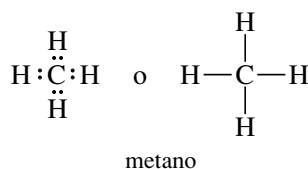
El **enlace covalente**, en el que se comparten electrones en lugar de transferirse, es la forma más habitual de enlace en los compuestos orgánicos. El hidrógeno, por ejemplo, necesita un segundo electrón para conseguir la configuración del gas noble helio. Si dos átomos de hidrógeno se unen y forman un enlace, «comparten» sus dos electrones y cada átomo tiene dos electrones en su capa de valencia.



El enlace covalente se estudiará con más detalle en el Capítulo 2.

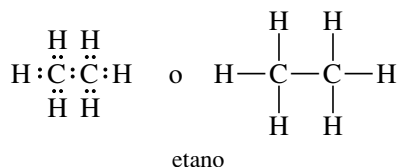
Una forma de simbolizar el enlace en una molécula covalente consiste en usar **estructuras de Lewis**. En una estructura de Lewis cada electrón de valencia se simboliza por un punto. Un par de electrones de enlace se simboliza por un par de puntos o por una línea (—). Se ha de intentar que todos los átomos tengan sus propias configuraciones de gas noble: dos electrones en el caso del hidrógeno y octetos para los elementos de la segunda fila de la tabla periódica.

Considere, por ejemplo, la estructura de Lewis del metano (CH_4):



El carbono contribuye con cuatro electrones de valencia y cada hidrógeno aporta uno, dando un total de ocho electrones. Todos estos ocho electrones rodean al carbono dando lugar a un octeto y cada átomo de hidrógeno comparte dos de los electrones.

La estructura de Lewis para el etano (C_2H_6) es más compleja:



Una vez más, se han colocado los electrones de valencia (14) y se han distribuido de forma que cada átomo de carbono quede rodeado por ocho electrones y cada hidrógeno por dos. La única estructura posible para el etano es la que se ha mostrado anteriormente, con los dos átomos de carbono compartiendo un par de electrones y cada átomo de hidrógeno compartiendo dos con uno de los carbonos. La estructura del etano muestra las características más importantes del carbono (su habilidad para formar enlaces fuertes carbono-carbono).

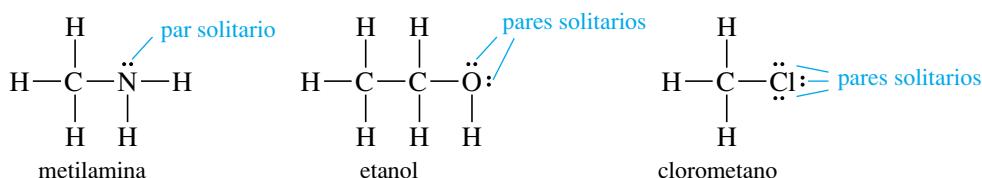
Los electrones de la capa de valencia que *no* son compartidos entre dos átomos reciben el nombre de **electrones no enlazantes**. Un par de electrones no enlazantes a menudo también es conocido como un **par solitario**. Los átomos de oxígeno, de nitrógeno y los halógenos (F, Cl, Br, I) normalmente tienen electrones no enlazantes en sus compuestos

1.4 Estructuras de Lewis

SUGERENCIA PARA RESOLVER PROBLEMAS

Las estructuras de Lewis son la forma de representar los enlaces en química orgánica. Aprender a representarlas de forma rápida y correctamente será muy útil a lo largo de este curso.

estables. Estos pares solitarios de electrones no enlazantes ayudan a determinar la reactividad de sus compuestos. Las estructuras de Lewis siguientes muestran un par solitario de electrones en el átomo de nitrógeno de la metilamina y dos pares solitarios en el átomo de oxígeno del etanol. Los átomos de los halógenos normalmente tienen tres pares solitarios, como se muestra en la estructura del clorometano.



Una estructura de Lewis correcta debería mostrar los pares solitarios de electrones. Los químicos orgánicos a menudo dibujan estructuras de Lewis omitiendo la mayoría o todos los pares solitarios de electrones. Éstas no son estructuras correctas de Lewis porque uno se ha de imaginar el número de electrones no enlazantes.

PROBLEMA 1.2

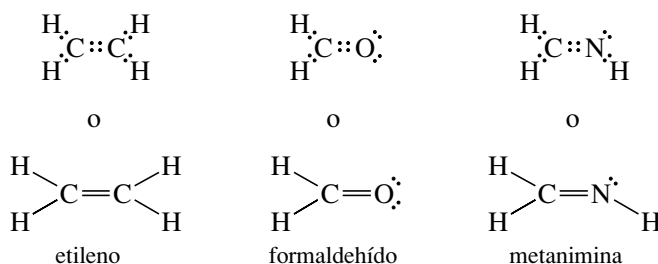
Dibuje las estructuras de Lewis de los siguientes compuestos:

- | | |
|--|--|
| (a) amoníaco, NH_3 | (b) agua, H_2O |
| (c) ión hidronio, H_3O^+ | (d) propano, C_3H_8 |
| (e) etilamina, $\text{CH}_3\text{CH}_2\text{NH}_2$ | (f) dimetil éter, CH_3OCH_3 |
| (g) fluoroetano, $\text{CH}_3\text{CH}_2\text{F}$ | (h) 2-propanol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ |
| (i) borano, BH_3 | (j) trifluoruro de boro, BF_3 |

Explique qué es inusual en el enlace de los compuestos (i) y (j).

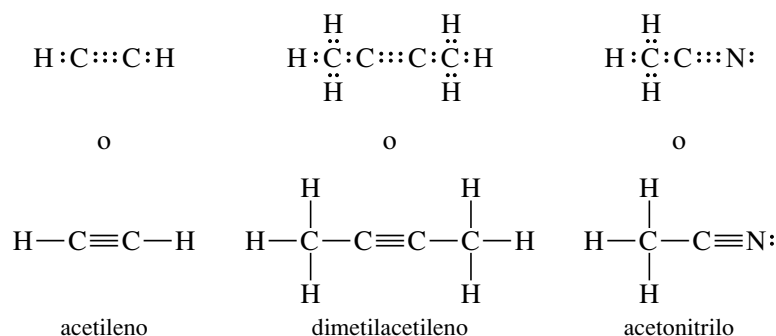
1.5 Enlace múltiple

Al representar las estructuras de Lewis en la Sección 1.4, se pusieron un par de electrones entre cada dos átomos. La compartición de un par de electrones entre dos átomos se conoce como **enlace sencillo**. Muchas moléculas comparten con sus átomos adyacentes dos o incluso tres pares de electrones; cuando se comparten dos pares se da el nombre de **enlace doble** y cuando se comparten tres pares se da el nombre de **enlace triple**. El etileno (C_2H_4) es un compuesto orgánico con un doble enlace. Cuando se representan las estructuras de Lewis para el etileno, la única forma de conseguir que los dos átomos de carbono tengan octetos es mediante la compartición de dos pares de electrones. El ejemplo siguiente muestra compuestos orgánicos con dobles enlaces. En cada caso, se comparten cuatro electrones (dos pares) entre dos átomos para formar octetos. Una doble línea (=) simboliza el doble enlace.



El acetileno, cuando se combina con el oxígeno, arde con una llama intensa que tiene diversas aplicaciones. Se puede utilizar para soldar las piezas de un puente bajo el agua o para reparar las tuberías de un oleoducto en Siberia.

El acetileno (C_2H_2) tiene un triple enlace. Su estructura de Lewis muestra los tres pares de electrones entre los dos átomos de carbono para que formen un octeto. Una línea triple (\equiv) simboliza el triple enlace.



Todas estas estructuras de Lewis muestran que el carbono normalmente forma cuatro enlaces en compuestos orgánicos neutros. El nitrógeno generalmente forma tres enlaces y el oxígeno dos. El hidrógeno y los halógenos normalmente forman un enlace. El número de enlaces que normalmente puede formar un átomo se conoce como **valencia**. El carbono es tetravalente, el nitrógeno trivalente, el oxígeno divalente, y el hidrógeno y los halógenos monovalentes. Si se recuerda el número usual de enlaces de estos elementos, se podrán escribir estructuras orgánicas con mucha facilidad. Si una estructura se representa de forma que cada átomo tenga el número de enlaces que le corresponden, la estructura de Lewis será correcta.

RESUMEN Modelos de enlace más frecuentes (sin carga)

	$\begin{array}{c} \\ -\text{C}- \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ -\text{N}- \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ -\text{O}- \\ \cdot\cdot \end{array}$	$-\text{H}$	$\begin{array}{c} \cdot\cdot \\ -\text{Cl}: \end{array}$
	carbono	nitrógeno	oxígeno	hidrógeno	halógenos
valencia:	4	3	2	1	1
pares solitarios:	0	1	2	0	3

SUGERENCIA PARA RESOLVER PROBLEMAS

Estos «números de enlaces usuales» pueden ser sencillos o estar combinados en dobles y triples enlaces. Por ejemplo, los tres enlaces del nitrógeno podrían corresponder a tres enlaces sencillos, a un enlace sencillo y uno doble, o a un triple enlace ($:\text{N}\equiv\text{N}:$). En los problemas hay que considerar todas las posibilidades.

PROBLEMA 1.3

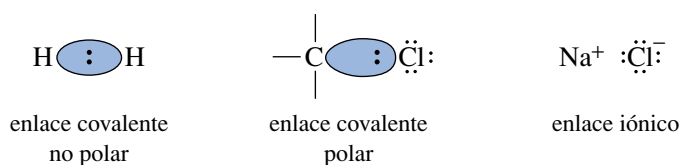
Escriba la estructura de Lewis para cada una de las siguientes fórmulas moleculares:

- | | | |
|---|---|----------------------------|
| (a) N_2 | (b) HCN | (c) HONO |
| (d) CO_2 | (e) H_2CNH | (f) HCO_2H |
| (g) $\text{C}_2\text{H}_3\text{Cl}$ | (h) HNNH | (i) C_3H_6 |
| (j) C_3H_4 (dos dobles enlaces) | (k) C_3H_4 (un triple enlace) | |

PROBLEMA 1.4

Rodee con un círculo los pares solitarios (pares de electrones no enlazantes) en las estructuras representadas en el Problema 1.3.

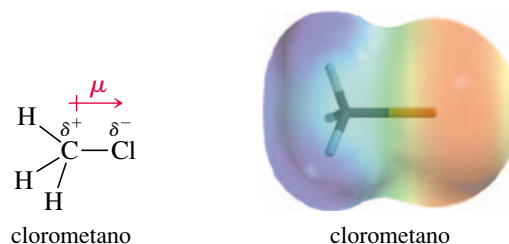
Un enlace cuyos electrones están igualmente compartidos por los dos átomos recibe el nombre de **enlace covalente no polar**. El enlace en la molécula de H_2 y el enlace $\text{C}-\text{C}$ en el etano son enlaces covalentes no polares. En la mayoría de enlaces entre dos elementos diferentes los electrones del enlace están atraídos de forma diferente por cada uno de los dos núcleos. Cuando la compartición del par de electrones del enlace no es igual para los dos átomos, a este enlace se le conoce como **enlace covalente polar**.



1.6 La electronegatividad y la polaridad de enlace

► **Figura 1.6**

El clorometano contiene un enlace polar carbono-cloro con una carga negativa parcial en el cloro y una carga positiva parcial en el carbono. El mapa de potencial electrostático muestra una región roja (rica en electrones) alrededor de la carga negativa parcial y una región azul (pobre en electrones) alrededor de la carga positiva parcial. El resto de colores indican valores intermedios de potencial electrostático.



Cuando el carbono se enlaza al cloro, por ejemplo, los electrones de enlace son atraídos más fuertemente hacia el átomo de cloro, por lo que el átomo de carbono adquirirá una pequeña carga positiva parcial y el átomo de cloro esa misma cantidad de carga pero de signo negativo. La Figura 1.6 muestra el enlace polar carbono-cloro del clorometano. Nosotros simbolizaremos la polaridad de enlace por una flecha que tenga como origen la carga positiva del enlace polar, y sobre este origen un signo positivo. La polaridad de un enlace se mide por su **momento dipolar** (μ), definido por el producto de la carga (separación de las cargas δ^+ y δ^-) y la longitud del enlace. El símbolo δ^+ significa «una pequeña cantidad de carga positiva» y el símbolo δ^- «una pequeña cantidad de carga negativa».

La Figura 1.6 también muestra un **mapa de potencial electrostático (MPE)** para el clorometano, que usa colores para representar la distribución de la carga calculada en una molécula. El rojo indica regiones ricas en electrones y el azul regiones pobres en electrones. El naranja, amarillo y verde indican niveles intermedios de potencial electrostático. En el clorometano, la región roja muestra la carga negativa parcial del cloro y la región azul indica la carga positiva parcial de los átomos de carbono y de hidrógeno.

A menudo se usan las **electronegatividades** como guía para predecir si un determinado enlace será polar y la dirección del momento dipolar. La escala de electronegatividad de Pauling, la que comúnmente utilizan los químicos orgánicos, se basa en las propiedades del enlace y es muy útil para predecir la polaridad de los enlaces covalentes. Los elementos con electronegatividades más altas atraen con más fuerza a los electrones de enlace. No obstante, en un enlace entre dos átomos diferentes, el átomo con la electronegatividad más alta es el extremo negativo del dipolo. La Figura 1.7 muestra las electronegatividades de Pauling para algunos de los elementos importantes de los compuestos orgánicos.

Obsérvese que la electronegatividad aumenta de izquierda a derecha a lo largo de la tabla periódica. El nitrógeno, el oxígeno y los halógenos son más electronegativos que el carbono; el sodio, el litio y el magnesio son menos electronegativos. La electronegatividad del hidrógeno es parecida a la del carbono, por lo que el enlace C—H normalmente se considera no polar. La polaridad de los enlaces y de las moléculas se tratará con más detalle en la Sección 2.9.

PROBLEMA 1.5

Haga uso de las electronegatividades para predecir los momentos dipolares de los siguientes enlaces:

- (a) C—Cl (b) C—O (c) C—N (d) C—S (e) C—B
(f) N—Cl (g) N—O (h) N—S (i) N—B (j) B—Cl

► **Figura 1.7**

Electronegatividades de algunos de los elementos que se encuentran en los compuestos orgánicos.

H 2.2						
Li 1.0	Be 1.6	B 1.8	C 2.5	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8						Br 3.0
						I 2.7

En los enlaces polares, las cargas parciales (δ^+ y δ^-) de los átomos del enlace son *reales*. Las **cargas formales** proporcionan un método de seguimiento de los electrones, pero pueden corresponder o no a cargas reales. En la mayoría de los casos, si la estructura de Lewis muestra que un átomo tiene una carga formal, quiere decir que tiene parte de esa carga. El concepto de carga formal ayuda a determinar qué átomos tienen mayor cantidad de carga en una molécula y ver que hay átomos cargados en moléculas que son neutras globalmente.

Para calcular las cargas formales, hay que contar cuántos electrones contribuyen a la carga de cada átomo y comparar ese número con el número de electrones de valencia que hay en el átomo neutro y aislado (dado por el número de grupo en la tabla periódica). Los electrones que contribuyen a la carga de un átomo son:

1. *Todos* sus electrones no compartidos (no enlazantes).
2. *La mitad* de los electrones (enlazantes) que comparte con otros átomos, o un electrón de cada par de enlace.

La carga formal de un átomo determinado puede ser calculada mediante la fórmula:

$$\text{carga formal (CF)} = [\text{número de grupo}] - [\text{electrones no enlazantes}] - \frac{1}{2}[\text{electrones compartidos}]$$

PROBLEMA RESUELTO 1.1

Calcule la carga formal (CF) de cada átomo de las estructuras siguientes:

(a) Metano (CH_4)

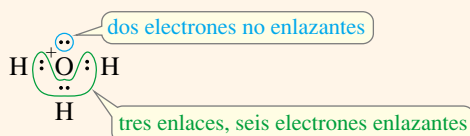


SOLUCIÓN

Cada átomo de hidrógeno del metano tiene un par enlazante de electrones (dos electrones compartidos). La mitad de los dos electrones compartidos es un electrón de valencia y es lo que el hidrógeno necesita para ser neutro. Los átomos de hidrógeno con un enlace son neutros formalmente: $\text{CF} = 1 - 0 - 1 = 0$.

El átomo de carbono tiene cuatro pares de electrones enlazantes (ocho electrones). La mitad de los ocho electrones compartidos, esto es, cuatro electrones son los que el carbono (grupo IVA) necesita para ser neutro. El carbono es formalmente neutro cuando tiene cuatro enlaces: $\text{CF} = 4 - 0 - \frac{1}{2}(8) = 0$.

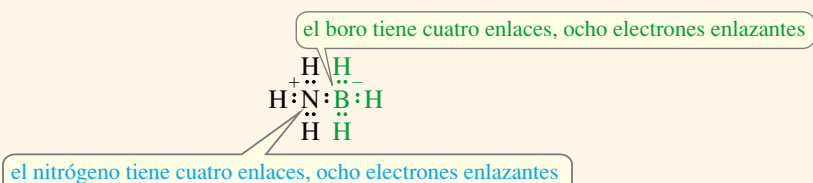
(b) Ión hidronio, H_3O^+



SOLUCIÓN

Cuando se representa la estructura de Lewis para este ión, se utilizan ocho electrones: seis del oxígeno y tres de los hidrógenos, menos uno porque el ión tiene una carga positiva. Cada hidrógeno tiene un enlace y es formalmente neutro. El oxígeno está rodeado por un octeto, con seis electrones enlazantes y dos electrones no enlazantes. La mitad de los electrones enlazantes más todos los electrones no enlazantes contribuyen a la carga: $6/2 + 2 = 5$; pero el oxígeno (grupo VIA) necesita seis electrones de valencia para ser neutro, por este motivo, el átomo de oxígeno tiene una carga formal de $+1$: $\text{CF} = 6 - 2 - \frac{1}{2}(6) = +1$.

(c) $\text{H}_3\text{N} - \text{BH}_3$



1.7 Cargas formales

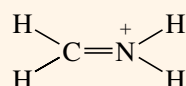
SOLUCIÓN

Éste es un compuesto neutro donde los átomos individuales están cargados formalmente. La estructura de Lewis muestra que tanto el nitrógeno como el boro tienen cuatro pares de electrones enlazantes. Los dos átomos, boro y nitrógeno, tienen $8/2 = 4$ electrones que contribuyen a sus cargas. El nitrógeno (grupo V) necesita cinco electrones de valencia para ser neutro, por lo que su carga formal es $+1$. El boro (grupo III) sólo necesita tres electrones de valencia para ser neutro, por lo que su carga formal es -1 .

$$\text{Nitrógeno: } CF = 5 - 0 - \frac{1}{2}(8) = +1$$

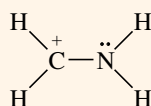
$$\text{Boro: } CF = 3 - 0 - \frac{1}{2}(8) = -1$$

(d) $[\text{H}_2\text{CNH}_2]^+$

**SOLUCIÓN**

En esta estructura, tanto el carbono como el nitrógeno tienen cuatro pares de electrones enlazantes. Con cuatro enlaces, el carbono es formalmente neutro; no obstante, el nitrógeno es del grupo V, por lo que su carga positiva formal es: $CF = 5 - 0 - 4 = +1$.

Este compuesto también podría ser representado con la siguiente estructura de Lewis:



En esta estructura, el átomo de carbono tiene tres enlaces con seis electrones enlazantes que, si se dividen entre dos, $6/2 = 3$, se observa que el carbono tiene un electrón menos de los cuatro que necesita para ser neutro formalmente: $CF = 4 - 0 - \frac{1}{2}(6) = +1$.

El nitrógeno tiene seis electrones enlazantes y dos electrones no enlazantes. Si se hace el cálculo $6/2 + 2 = 5$, se observa que el nitrógeno es neutro en esta segunda estructura:

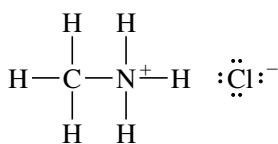
$$CF = 5 - 2 - \frac{1}{2}(6) = 0$$

El significado de estas dos estructuras de Lewis se discute en la Sección 1.9.

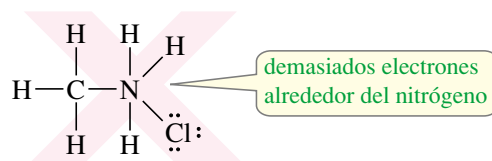
La mayoría de los compuestos orgánicos sólo contienen un número pequeño de elementos bastante comunes, normalmente con el octeto de electrones completo. La tabla resumen de la página siguiente indica la naturaleza de los enlaces más habituales, utilizando líneas para representar los pares de electrones enlazantes. Utilice estas reglas de cálculo de las cargas formales para comprobar las cargas que se dan en las estructuras. Si las estructuras se entienden bien, será fácil representar los compuestos orgánicos y sus iones de forma rápida y correcta.

1.8 Estructuras iónicas

Algunos compuestos orgánicos contienen enlaces iónicos. Por ejemplo, la estructura del cloruro de metilamonio ($\text{CH}_3\text{NH}_3\text{Cl}$) no se puede representar si solamente se utilizan enlaces covalentes; esto requeriría que el nitrógeno tuviese cinco enlaces, lo que implicaría diez electrones en la capa de valencia. La estructura correcta contiene un ión cloruro enlazado iónicamente al resto de la estructura.



cloruro de metilamonio



no se puede representar mediante enlaces covalentes

RESUMEN

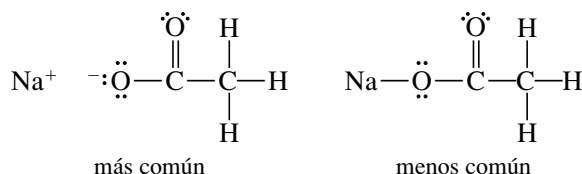
Modelos de enlace más frecuentes en los compuestos e iones orgánicos

Átomo	Electrones de valencia	Cargado positivamente	Neutro	Cargado negativamente
B	3		(no octeto) $\begin{array}{c} \text{—B—} \\ \end{array}$	$\begin{array}{c} \\ \text{—B—} \\ \end{array}$
C	4	$\begin{array}{c} + \\ \text{—C—} \\ \end{array}$ (no octeto)	$\begin{array}{c} \\ \text{—C—} \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—C—} \\ \end{array}$
N	5	$\begin{array}{c} \\ \text{—N}^+ \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—N—} \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—N—} \\ \end{array}$
O	6	$\begin{array}{c} \cdot\cdot \\ \text{—O}^+ \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—O—} \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—O—} \\ \end{array}$
halógeno	7	$\begin{array}{c} \cdot\cdot \\ \text{—Cl}^+ \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—Cl:} \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{:Cl:}^- \end{array}$

SUGERENCIA
PARA RESOLVER PROBLEMAS

Esta tabla es muy importante. Haz un número de problemas suficientes como para familiarizarte con estos modelos de enlace, tal que puedas saber cuándo otros modelos son incorrectos o bien inusuales.

Algunas moléculas se pueden representar tanto en forma covalente como iónica. Por ejemplo, el acetato de sodio (NaOCOCH_3) se puede representar tanto con un enlace covalente como con un enlace iónico entre el sodio y el oxígeno. Como el sodio normalmente forma enlaces iónicos con el oxígeno (NaOH), la estructura con enlace iónico es la que se prefiere. En general, los enlaces entre átomos con gran diferencia de electronegatividad (2 o más) normalmente se representan como compuestos iónicos.



PROBLEMA 1.6

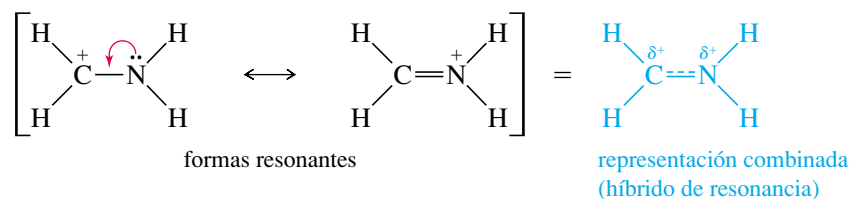
Dibuje las estructuras de Lewis de los siguientes compuestos e iones, diciendo cuál es su carga formal apropiada:

- | | |
|---|---------------------------------|
| (a) $[\text{CH}_3\text{OH}_2]^+$ | (b) NH_4Cl |
| (c) $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ | (d) NaOCH_3 |
| (e) $^+\text{CH}_3$ | (f) $^-\text{CH}_3$ |
| (g) NaBH_4 | (h) NaBH_3CN |
| (i) $(\text{CH}_3)_2\text{O—BF}_3$ | (j) $[\text{HONH}_3]^+$ |
| (k) $\text{KOC}(\text{CH}_3)_3$ | (l) $[\text{H}_2\text{C=OH}]^+$ |

1.9A Híbridos de resonancia

Algunas de las estructuras de los compuestos no es adecuado representarlas mediante una sola estructura de Lewis. Cuando son posibles dos o más estructuras de enlace de valencia, que difieren sólo en la colocación de los electrones, la molécula suele mostrar características de las dos estructuras. A estas estructuras diferentes se las conoce como **estructuras de resonancia** o **formas resonantes**, ya que no son compuestos diferentes, sino formas diferentes de representar el mismo compuesto. La molécula real se dice que corresponde a un **híbrido de resonancia** de sus formas resonantes. En el Problema resuelto 1.1(d) se mostró cómo el ión $[\text{H}_2\text{CNH}_2]^+$ se podía representar por cualquiera de las siguientes formas de resonancia:

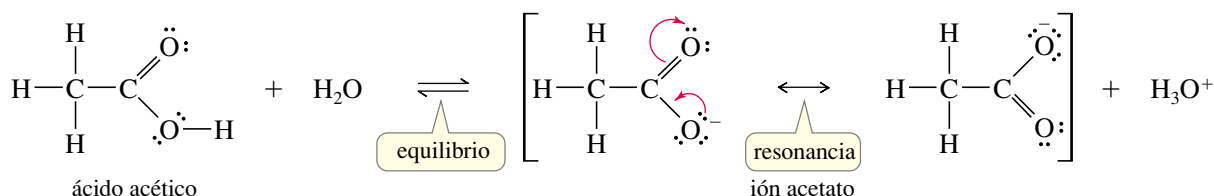
1.9
Resonancia



La estructura real de este ión es un híbrido de resonancia de las dos estructuras. En la molécula real, la carga positiva está **deslocalizada** (extendida) entre el átomo de carbono y el de nitrógeno. En la forma resonante de la izquierda, la carga positiva está en el carbono, pero el carbono no tiene un octeto. Los electrones no enlazantes del nitrógeno se pueden mover por el enlace (tal como indica la flecha roja) dando una segunda estructura con un doble enlace entre el nitrógeno que tiene carga positiva y el carbono que posee un octeto. La representación combinada de las dos formas de resonancia en una sola representación da lugar a una carga compartida entre el nitrógeno y el carbono.

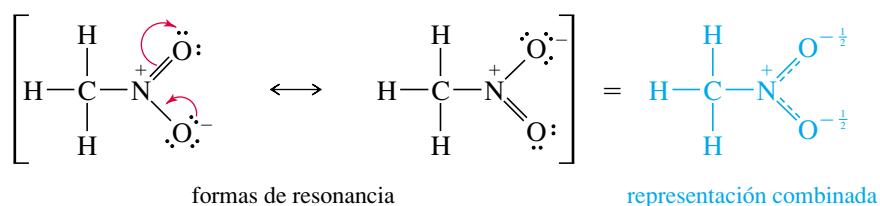
El extender la carga positiva sobre dos átomos hace que el ión sea más estable que en el caso de que la carga positiva estuviera localizada solamente sobre el carbono o sobre el nitrógeno. Se dice que este catión está **estabilizado por resonancia**. La resonancia es más importante cuando permite que una carga esté deslocalizada entre dos o más átomos, como en el ejemplo mencionado.

La estabilización por resonancia desempeña un papel crucial en la química orgánica, especialmente en la química de compuestos que tienen dobles enlaces. Se usará frecuentemente el concepto de resonancia a lo largo de este curso. Por ejemplo, la acidez del ácido acético (véase abajo) se incrementa por efecto de la resonancia. Cuando el ácido acético pierde un protón, el ión acetato resultante tiene una carga negativa deslocalizada sobre los dos átomos de oxígeno. Cada átomo de oxígeno posee la mitad de la carga negativa y su deslocalización estabiliza el ión. Cada uno de los enlaces carbono-oxígeno es intermedio entre un enlace doble y un enlace sencillo, por lo que se dice que su *orden de enlace* es de $1\frac{1}{2}$.



Se usará una sola flecha con doble punta entre las formas de resonancia (a menudo puestas entre corchetes) para indicar que la estructura real es un híbrido de las estructuras de Lewis representadas. Por otra parte, un equilibrio se representará por dos flechas con sentidos opuestos.

Algunas moléculas sin carga también tienen estructuras de resonancia estabilizadas con la misma carga formal positiva y negativa. Se pueden representar dos estructuras de Lewis para el nitrometano (CH_3NO_2), pero las dos estructuras tienen una carga positiva formal en el nitrógeno y una carga negativa en uno de los oxígenos. Por tanto, el nitrometano tiene una carga positiva en el átomo de nitrógeno y una carga negativa extendida por igual sobre los dos átomos de oxígeno. Los enlaces N—O están entre un enlace sencillo y uno doble, tal como se indica en la representación combinada siguiente:

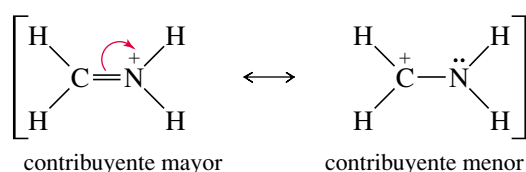


Recuerde que las formas de resonancia individuales no existen como especies químicas independientes. La molécula no «resuena» entre esas estructuras, es un híbrido con

características de ambas estructuras. Una analogía sería una mula, que es un híbrido de un caballo y un burro. La mula no «resuena» entre parecerse a un caballo o a un burro; simplemente es una mula, con el amplio dorso de un caballo y las grandes orejas de un burro.

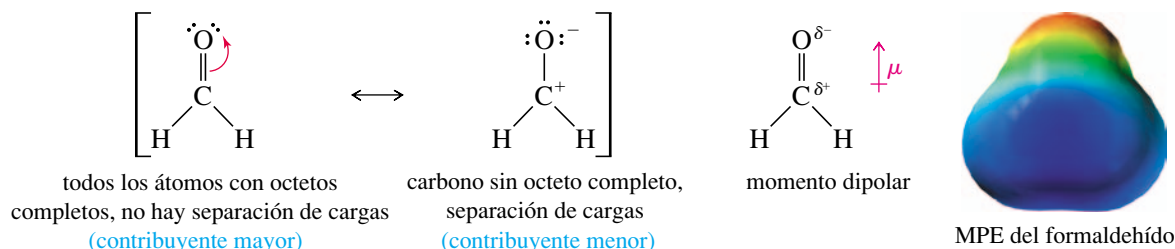
1.9B Contribución mayor o menor de las formas resonantes al híbrido de resonancia

Dos o más estructuras de Lewis correctas para un mismo compuesto pueden o no representar distribuciones de electrones de igual energía. A pesar de que formas de resonancia separadas no existen, se pueden estimar sus energías relativas como si existieran. La mayoría de las formas de resonancia estables son representaciones más cercanas de la molécula real que las menos estables. Las dos formas de resonancia del apartado anterior, para el ión acetato, tienen enlaces similares e idéntica energía. Lo mismo se puede decir para las dos formas de resonancia del nitrometano. Las formas de resonancia siguientes, por el contrario, tienen enlaces diferentes.



Las estructuras anteriores no tienen la misma energía estimada. La primera estructura tiene la carga positiva en el nitrógeno. La segunda tiene la carga positiva en el carbono, y el átomo de carbono no posee un octeto completo. La primera estructura es más estable ya que tiene un enlace adicional y todos los átomos tienen octetos completos. Muchos iones estables tienen una carga positiva en el átomo de nitrógeno con cuatro enlaces (*véase* la tabla resumen de la página 13). A la forma de resonancia más estable se la conoce como la **contribuyente mayor** y a la forma menos estable como la **contribuyente menor**. La estructura del compuesto real se parece más al contribuyente mayor que al contribuyente menor.

Muchas moléculas orgánicas tienen contribuyentes de resonancia mayor y menor. El formaldehído ($\text{H}_2\text{C}=\text{O}$) se puede representar con una carga negativa en el oxígeno, equilibrada por una carga positiva en el carbono. Esta forma de resonancia polar tiene mayor energía estimada que la estructura con doble enlace, porque tiene separación de cargas, menos enlaces y un átomo de carbono cargado positivamente con un octeto incompleto. La estructura con cargas separadas es solamente un contribuyente menor, pero ayuda a explicar por qué el enlace $\text{C}=\text{O}$ del formaldehído es muy polar, con una carga positiva parcial en el carbono y una carga negativa parcial en el oxígeno. El mapa de potencial electrostático (MPE) también muestra una región rica en electrones (rojo) alrededor del oxígeno y una región pobre en electrones (azul) alrededor del carbono en el formaldehído.



Cuando se representan las formas de resonancia, se intenta dibujar estructuras que sean lo más bajas posible en energía. Las mejores candidatas son las que tienen un número máximo de octetos y el máximo número de enlaces. Además, las estructuras tienen que tener la mínima cantidad de separación de cargas.

Sólo los electrones pueden estar deslocalizados. Al contrario que los electrones, los núcleos no pueden estar deslocalizados, deben permanecer en el mismo lugar, con las mismas distancias de enlace y los mismos ángulos en todos los contribuyentes a la resonancia. Las reglas generales siguientes serán útiles para representar estructuras de resonancias.

SUGERENCIA PARA RESOLVER PROBLEMAS

Para comparar las formas de resonancia se pueden utilizar los siguientes criterios, comenzando por el más importante:

1. Tantos octetos como sea posible.
2. Tantos enlaces como sea posible.
3. Si hay carga negativa se coloca en los átomos electronegativos.
4. La menor separación de cargas posible.

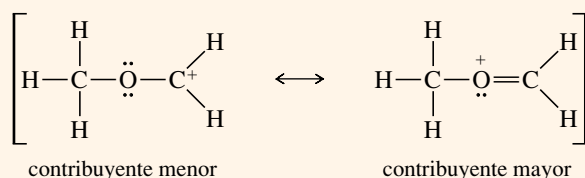
1. Todas las estructuras de resonancia deben ser estructuras de Lewis válidas para el compuesto.
2. Sólo se puede cambiar la posición de los electrones de una estructura a otra (los electrones de los dobles enlaces y pares solitarios son los que se cambian con más frecuencia). El núcleo no se puede cambiar de posición y los ángulos de enlace han de ser los mismos.
3. El número de electrones desapareados (si hay alguno) debe permanecer igual. La mayoría de los compuestos estables no tienen electrones desapareados y todos los electrones deben permanecer apareados en todas las estructuras de resonancia.
4. El contribuyente mayor a la resonancia es el que tiene menor energía.
Los buenos contribuyentes generalmente tienen todos los octetos satisfechos, con el máximo número de enlaces covalentes que sea posible y con una separación de cargas lo menor posible. Las cargas negativas son más estables en los átomos más electronegativos.
5. La estabilización por resonancia es más importante cuando sirve para deslocalizar una carga entre dos o más átomos.

PROBLEMA RESUELTO 1.2

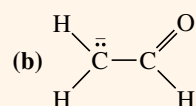
Para cada uno de los siguientes compuestos, represente las formas de resonancia importantes. Indique qué estructuras tienen contribuyentes mayores y menores, o si tienen la misma energía.

(a) $[\text{CH}_3\text{OCH}_2]^+$

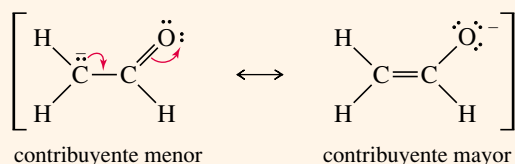
SOLUCIÓN



La primera estructura (menor) tiene un átomo de carbono con sólo seis electrones a su alrededor. La segunda estructura (mayor) tiene octetos en todos los átomos y un enlace adicional.



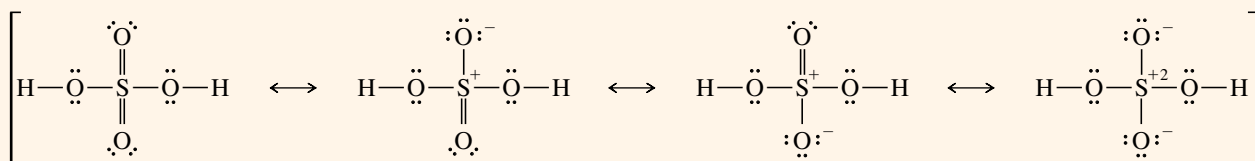
SOLUCIÓN



Las dos estructuras tienen octetos en el átomo de oxígeno y en el de carbono, y tienen el mismo número de enlaces. La primera estructura tiene la carga negativa en el carbono y la segunda la tiene en el oxígeno. El oxígeno es más electronegativo que el carbono, por lo tanto, la segunda estructura es el contribuyente mayor.

(c) H_2SO_4

SOLUCIÓN



La primera estructura, con más enlaces y menor separación de carga, es posible porque el azufre es un elemento de la tercera fila de la tabla periódica con orbitales *d* accesibles, lo que le da la posibilidad de expandir aparentemente su octeto. Por ejemplo, el SF_6 es un compuesto estable con 12 electrones alrededor del azufre. Sin embargo, algunos cálculos teóricos sugieren que la última estructura representada, con octetos en todos los átomos, podría ser la contribuyente mayor a la resonancia. No se puede predecir siempre el contribuyente mayor de un híbrido de resonancia.

PROBLEMA 1.7

Represente las formas de resonancia importantes de las siguientes moléculas e iones:

- (a) CO_3^{2-} (b) NO_3^- (c) NO_2^- (d) $\text{H}_2\text{C}=\text{CH}-\text{CH}_2^+$
 (e) $\text{H}_2\text{C}=\text{CH}-\text{CH}_2^-$ (f) SO_4^{2-} (g) $[\text{CH}_3\text{C}(\text{OCH}_3)_2]^+$

PROBLEMA 1.8

Para cada uno de los siguientes compuestos, represente las formas de resonancia importantes. Indique qué estructuras son las contribuyentes mayores y menores a la resonancia, o si tienen la misma energía.

- (a) $[\text{H}_2\text{CNO}_2]^-$ (b) $\text{H}_2\text{C}=\text{CH}-\text{NO}_2$ (c) $[\text{H}_2\text{COH}]^+$
 (d) H_2CNN (e) $[\text{H}_2\text{CCN}]^-$ (f) $\text{H}_2\text{N}-\overset{+}{\text{CH}}-\text{CH}=\text{CH}-\text{NH}_2$
 (g) $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{-}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ (h) $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$

SUGERENCIA**PARA RESOLVER PROBLEMAS**

Quando se representan formas de resonancia para iones, observe cómo se puede deslocalizar la carga entre varios átomos. Intente colocar una carga negativa sobre elementos electronegativos como el oxígeno y el nitrógeno. Intente, así mismo, colocar una carga positiva sobre todos los carbonos que sea posible, pero especialmente sobre los átomos que puedan alojar la carga positiva y tener un octeto completo; por ejemplo, el oxígeno (con tres enlaces) o el nitrógeno (con cuatro enlaces).

Los químicos orgánicos utilizan varias clases de fórmulas para representar los compuestos orgánicos. Algunas de estas fórmulas incluyen una notación específica que requiere una explicación. Las **fórmulas estructurales** indican qué átomos están enlazados a otros. Hay dos tipos de fórmulas estructurales: las estructuras de Lewis completas y las fórmulas estructurales condensadas. Además, hay varias formas de representar fórmulas estructurales condensadas. Según se ha visto, una estructura de Lewis simboliza un par de electrones enlazantes como un par de puntos o como una línea (—). Los pares solitarios de electrones se muestran como pares de puntos.

1.10**Fórmulas estructurales****1.10A Fórmulas estructurales condensadas**

Las **fórmulas estructurales condensadas** (Tabla 1.2) se representan sin mostrar todos los enlaces individuales. En una estructura condensada, cada átomo central se representa junto a los átomos a los que está enlazado. Los átomos enlazados a un átomo central a menudo se escriben a continuación del átomo central (CH_3CH_3 en lugar de $\text{H}_3\text{C}-\text{CH}_3$) incluso aunque no sea el orden del verdadero enlace. En muchos casos, si hay dos o más grupos idénticos, se puede utilizar un paréntesis y un subíndice para representar a todos estos grupos. Los electrones no enlazantes raramente se representan en las fórmulas estructurales condensadas.

TABLA 1.2 Ejemplos de fórmulas estructurales condensadas

Compuesto	Estructura de Lewis	Fórmula estructural condensada
etano	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$	CH_3CH_3
isobutano	$\begin{array}{c} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C} & -\text{C}- & \text{C}-\text{H} \\ & & \\ \text{H} & & \text{H} \\ & & \\ & \text{H}-\text{C}-\text{H} \\ & & \\ & \text{H} & \end{array}$	$(\text{CH}_3)_3\text{CH}$
n-hexano	$\begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$

(continúa en la página siguiente)

TABLA 1.2 (continuación)

Compuesto	Estructura de Lewis	Fórmula estructural condensada
dietil éter	$ \begin{array}{ccccccc} & \text{H} & \text{H} & & \text{H} & \text{H} & \\ & & & & & & \\ \text{H} & - \text{C} & - \text{C} & - \ddot{\text{O}} & - \text{C} & - \text{C} & - \text{H} \\ & & & & & & \\ & \text{H} & \text{H} & & \text{H} & \text{H} & \end{array} $	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ o $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$ o $(\text{CH}_3\text{CH}_2)_2\text{O}$
etanol	$ \begin{array}{ccccccc} & \text{H} & \text{H} & & & & \\ & & & & & & \\ \text{H} & - \text{C} & - \text{C} & - \ddot{\text{O}} & - \text{H} \\ & & & & & & \\ & \text{H} & \text{H} & & & & \end{array} $	$\text{CH}_3\text{CH}_2\text{OH}$
alcohol isopropílico	$ \begin{array}{ccccccc} & \text{H} & & \ddot{\text{O}} & - \text{H} & \text{H} & \\ & & & & & & \\ \text{H} & - \text{C} & - \text{C} & - & \text{C} & - \text{H} \\ & & & & & \\ & \text{H} & \text{H} & & \text{H} & \end{array} $	$(\text{CH}_3)_2\text{CHOH}$
dimetilamina	$ \begin{array}{ccccccc} & \text{H} & & & \text{H} & & \\ & & & & & & \\ \text{H} & - \text{C} & - \ddot{\text{N}} & - & \text{C} & - \text{H} \\ & & & & & \\ & \text{H} & & & \text{H} & \end{array} $	$(\text{CH}_3)_2\text{NH}$

Cuando se escribe una fórmula estructural condensada para un compuesto que contiene enlaces dobles o triples, los enlaces múltiples con frecuencia se representan igual que en las estructuras de Lewis. La Tabla 1.3 muestra ejemplos de fórmulas estructurales condensadas que contienen enlaces múltiples. Observe que el grupo $-\text{CHO}$ de un aldehído y el grupo $-\text{COOH}$ de un ácido carboxílico se enlazan de forma diferente a como sugiere la notación condensada.

Como se puede observar en las Tablas 1.2 y 1.3, la diferencia entre una fórmula estructural de Lewis completa y una fórmula estructural condensada puede ser confusa. Los químicos con frecuencia representan las fórmulas con algunas partes condensadas y otras

TABLA 1.3 Fórmulas estructurales condensadas para dobles y triples enlaces

Compuesto	Estructura de Lewis	Fórmula estructural condensada
2-buteno	$ \begin{array}{ccccccc} & \text{H} & \text{H} & & \text{H} & & \\ & & & & & & \\ \text{H} & - \text{C} & - \text{C} = \text{C} & - \text{C} & - \text{H} \\ & & & & & \\ & \text{H} & & \text{H} & \text{H} & \end{array} $	$\text{CH}_3\text{CHCHCH}_3$ o $\text{CH}_3\text{CH}=\text{CHCH}_3$
acetonitrilo	$ \begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{C} \equiv \text{N} : \\ \\ \text{H} \end{array} $	CH_3CN o $\text{CH}_3\text{C} \equiv \text{N}$
acetaldehído	$ \begin{array}{c} \text{H} \quad \ddot{\text{O}} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \\ \text{H} \end{array} $	CH_3CHO o $\text{CH}_3\overset{\text{O}}{\underset{ }{\text{C}}}\text{H}$
acetona	$ \begin{array}{c} \text{H} \quad \ddot{\text{O}} \quad \text{H} \\ \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} $	CH_3COCH_3 o $\text{CH}_3\overset{\text{O}}{\underset{ }{\text{C}}}\text{CH}_3$
ácido acético	$ \begin{array}{c} \text{H} \quad \ddot{\text{O}} \\ \quad \\ \text{H} - \text{C} - \text{C} - \ddot{\text{O}} - \text{H} \\ \\ \text{H} \end{array} $	CH_3COOH o $\text{CH}_3\overset{\text{O}}{\underset{ }{\text{C}}}-\text{OH}$ o $\text{CH}_3\text{CO}_2\text{H}$

completamente desarrolladas. El estudiante debería trabajar con las diferentes formas de representar las fórmulas para entender su significado.

PROBLEMA 1.9

Represente las estructuras de Lewis completas para las siguientes fórmulas estructurales condensadas:

- (a) $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_3)_2$ (b) $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$ (c) $\text{CH}_3\text{CH}_2\text{COCHCH}_2$
 (d) $\text{CH}_3\text{CH}_2\text{CHO}$ (e) CH_3COCN (f) $(\text{CH}_3)_3\text{CCOOH}$ (g) $(\text{CH}_3\text{CH}_2)_2\text{CO}$

1.10B Fórmulas lineoangulares

Otra forma de representar las estructuras orgánicas es la **fórmula lineoangular**, algunas veces llamada **estructura esquelética** o de barras. Las fórmulas lineoangulares con frecuencia se usan en los compuestos cíclicos y muy ocasionalmente en los lineales. En una fórmula lineoangular, los enlaces están representados por líneas y los átomos de carbono vienen dados por los vértices o puntos de encuentro de dos líneas, o el punto del principio o final de la línea en el caso de los extremos. Los átomos de nitrógeno, de oxígeno y los halógenos se escriben con su símbolo, pero los átomos de hidrógeno frecuentemente no se simbolizan a no ser que vayan unidos a elementos que se han simbolizado. Se supone que cada átomo de carbono tiene los suficientes átomos de hidrógeno para que el total de sus enlaces sea cuatro. Los electrones no enlazantes raramente se representan. La Tabla 1.4 muestra algunos ejemplos de estas representaciones lineoangulares.

TABLA 1.4 Ejemplos de representaciones lineoangulares

Compuesto	Estructura condensada	Fórmula lineoangular
hexano	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	
2-hexeno	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3$	
3-hexanol	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_3$	
2-ciclohexenona		
2-metilciclohexanol		
ácido nicotínico (vitamina, también llamada niacina)		

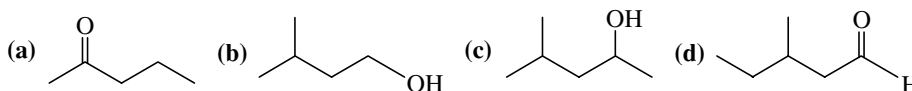
PROBLEMA 1.10

Escriba la estructura de Lewis correspondiente a las siguientes estructuras lineoangulares:

- (a)
- (b)
- (c)
- (d)
- (e)
- (f)
- (g)
- (h)

PROBLEMA 1.11

Represente las fórmulas estructurales condensadas correspondientes a las siguientes estructuras lineoangulares:



1.11

Fórmulas moleculares y fórmulas empíricas

Antes de poder escribir las posibles fórmulas estructurales de un compuesto, se necesita saber su fórmula molecular. La **fórmula molecular** simplemente informa del número de átomos de cada elemento que hay en una molécula de un compuesto. Por ejemplo, la fórmula molecular del 1-butanol es $C_4H_{10}O$.



1-butanol, fórmula molecular $C_4H_{10}O$

Cálculo de la fórmula empírica Las fórmulas moleculares se pueden determinar mediante un proceso que consta de dos pasos. El primer paso es la determinación de la **fórmula empírica**, o relación relativa entre los elementos presentes en la molécula. Suponga, por ejemplo, que en un compuesto desconocido, por análisis elemental cuantitativo, se encontró que contenía un 40.00% de carbono y un 6.67% de hidrógeno. La masa restante, 53.33%, se supone que era oxígeno. Para pasar esos números a una fórmula empírica, se puede seguir un procedimiento simple:

1. Suponga que la muestra contiene 100 g, por lo que los valores porcentuales dan el número de gramos de cada elemento. Dividiendo el número de gramos de cada elemento por la masa atómica se obtiene el número de moles de ese átomo en los 100 g de muestra.
2. Divida cada uno de los números de moles obtenidos en el paso anterior por el número más pequeño y redondee a la cifra entera más próxima. Este paso ha de conducir a la relación existente, expresada en números enteros, entre los elementos de la molécula.

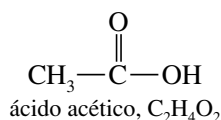
Para el compuesto desconocido, con los datos anteriores y siguiendo los pasos indicados, se obtendrían los siguientes resultados:

$$\begin{array}{lcl} \frac{40.0 \text{ g C}}{12.0 \text{ g/mol}} = 3.33 \text{ mol C;} & \frac{3.33 \text{ mol}}{3.33 \text{ mol}} = 1 \\ \frac{6.67 \text{ g H}}{1.01 \text{ g/mol}} = 6.60 \text{ mol H;} & \frac{6.60 \text{ mol}}{3.33 \text{ mol}} = 1.98 \approx 2 \\ \frac{53.3 \text{ g O}}{16.0 \text{ g/mol}} = 3.33 \text{ mol O;} & \frac{3.33 \text{ mol}}{3.33 \text{ mol}} = 1 \end{array}$$

En el primer cálculo se divide el número de gramos de carbono por 12, el número de gramos de hidrógeno por 1 y el número de gramos de oxígeno por 16. Se comparan los resultados dividiendo todos los valores obtenidos por el número más pequeño, 3.33. El resultado final da una relación de un átomo de carbono por dos de hidrógeno y uno de oxígeno. Este resultado nos dice que la fórmula empírica es $C_1H_2O_1$ o CH_2O , que muestra solamente la relación de los elementos. La fórmula molecular puede ser un múltiplo cualquiera de la fórmula empírica, porque cualquier múltiplo también tiene la misma relación numérica entre los átomos de sus elementos. Fórmulas moleculares posibles son CH_2O , $C_2H_4O_2$, $C_3H_6O_3$, $C_4H_8O_4$, etc.

Cálculo de la fórmula molecular ¿Cómo se sabe cuál es la fórmula molecular correcta? Se puede elegir el verdadero múltiplo de la fórmula empírica cuando se conoce la masa molecular. Las masas moleculares de una sustancia se pueden determinar por métodos como el *descenso crioscópico* o el *aumento ebulloscópico* de un disolvente cuando contiene la sustancia desconocida a una concentración molar. Si el compuesto es volátil, se puede convertir en gas y utilizar su volumen para determinar el número de moles por la *ley de los gases ideales*. En la actualidad existen métodos entre los que se incluye la *espectrometría de masas*, que será tratada en el Capítulo 11.

Para el ejemplo anterior (fórmula empírica: CH_2O) supondremos que la masa molecular es aproximadamente 60. La masa de una unidad de CH_2O es 30, por lo que el compuesto contendrá el doble número de átomos. La fórmula molecular será $\text{C}_2\text{H}_4\text{O}_2$. Este compuesto podría ser el ácido acético.



En los Capítulos 12, 13 y 15 se usarán técnicas espectroscópicas para determinar la estructura completa de un compuesto una vez que se conozca su fórmula molecular.

PROBLEMA 1.12

Escriba la fórmula empírica y la fórmula molecular a partir de los análisis elementales siguientes. En cada caso, proponga al menos una estructura que corresponda a la fórmula molecular.

	C	H	N	Cl	PM(*)
(a)	40.0%	6.67%	0	0	90
(b)	32.0%	6.67%	18.7%	0	75
(c)	37.2%	7.75%	0	55.0%	64
(d)	38.4%	4.80%	0	56.8%	125

(*) Peso molecular.

SUGERENCIA

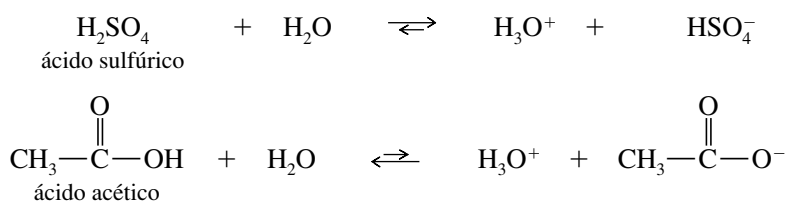
PARA RESOLVER PROBLEMAS

Si un análisis elemental no suma el 100%, el porcentaje que falta se supone que es de oxígeno.

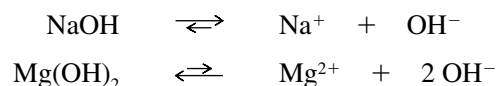
Las propiedades y la reactividad de los ácidos y de las bases son fundamentales para el estudio de la química orgánica. Hay que saber exactamente qué quieren decir los términos **ácido** y **base**. La mayoría de la gente estaría de acuerdo en que el H_2SO_4 es un ácido y el NaOH una base. ¿El BF_3 es un ácido o es una base? ¿El etileno ($\text{H}_2\text{C}=\text{CH}_2$) es un ácido o una base? Para responder a estas preguntas se necesitan entender las tres definiciones diferentes de los ácidos y de las bases: la definición de Arrhenius, la de Brønsted-Lowry y la de Lewis.

La primera clasificación de los compuestos ácidos se hizo basándose en su sabor agrio. Los términos latinos *acidus* (agrio) y *acetum* (vinagre) dieron lugar a los términos actuales de *ácido* y *ácido acético*. Los compuestos alcalinos (bases) eran sustancias que neutralizaban a los ácidos, tales como la caliza y las cenizas de las plantas (en árabe, *al kalai*).

La *teoría de Arrhenius* se desarrolló al final del siglo diecinueve y definía los ácidos como sustancias que se disocian en el agua para formar iones H_3O^+ . Se asumió que los ácidos más fuertes, tales como el ácido sulfúrico (H_2SO_4), se disociaban mucho más que los ácidos débiles, tales como el ácido acético (CH_3COOH).



Según la definición de Arrhenius, las bases son sustancias que se disocian en solución acuosa para formar iones hidroxilo. Por otra parte se consideró que las bases fuertes, tales como el NaOH , se disociaban más que las débiles o que aquellas que se disuelven moderadamente, como el $\text{Mg}(\text{OH})_2$.



La acidez o basicidad de una solución acuosa (agua) de una sustancia se mide por la concentración de H_3O^+ en dicha disolución. Este valor también permite conocer implícitamente la concentración de OH^- , ya que estas dos concentraciones están relacionadas entre sí por la constante de ionización del agua:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad (\text{a } 24^\circ\text{C})$$

1.12

Ácidos y bases de Arrhenius

En las soluciones neutras la concentración de $[\text{H}_3\text{O}^+]$ y de $[\text{OH}^-]$ son iguales,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M} \text{ en una solución neutra}$$

Las soluciones ácidas y básicas poseen un exceso de $[\text{H}_3\text{O}^+]$ o de $[\text{OH}^-]$, respectivamente.

$$\text{ácidas: } [\text{H}_3\text{O}^+] > 10^{-7} \text{ M} \text{ y } [\text{OH}^-] < 10^{-7} \text{ M}$$

$$\text{básicas: } [\text{H}_3\text{O}^+] < 10^{-7} \text{ M} \text{ y } [\text{OH}^-] > 10^{-7} \text{ M}$$

Como estas concentraciones pueden abarcar un amplio rango de valores, la acidez o basicidad de una solución normalmente se mide en escala logarítmica. El **pH** se define como el logaritmo (en base 10), cambiado de signo, de la concentración de H_3O^+ .

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

Una solución neutra tiene un pH de 7, una solución ácida tiene un pH menor que 7 y una solución básica tiene un pH mayor que 7.

PROBLEMA 1.13

Calcule el pH de las siguientes soluciones:

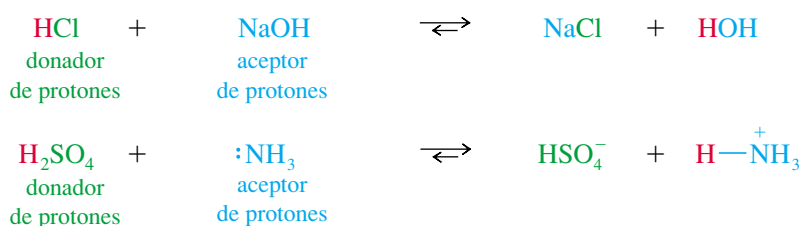
- (a) 5.00 g de HBr en 100 mL de solución acuosa.
- (b) 1.50 g de NaOH en 50 mL de solución acuosa.

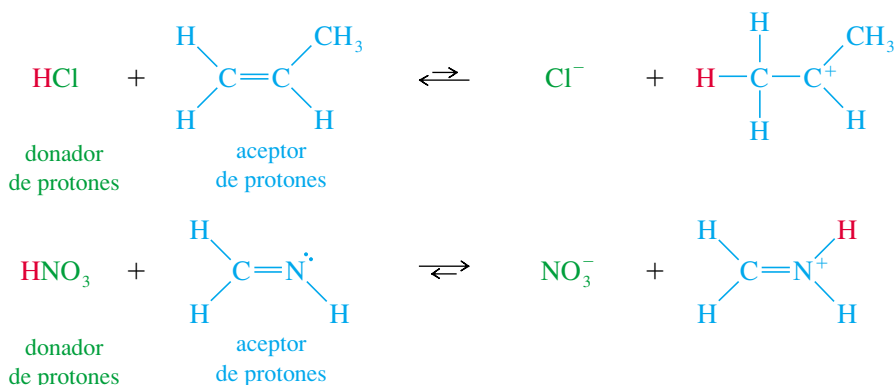
La definición de Arrhenius fue una contribución importante para poder entender muchos ácidos y muchas bases, pero no explica por qué un compuesto como el amoníaco (NH_3) neutraliza los ácidos, a pesar de no tener un ión hidróxido en su fórmula molecular. En la Sección 1.13 se explica una teoría más versátil de ácidos y bases que incluye al amoníaco y a una variedad más amplia de ácidos y bases orgánicos.

1.13 Ácidos y bases de Brønsted-Lowry

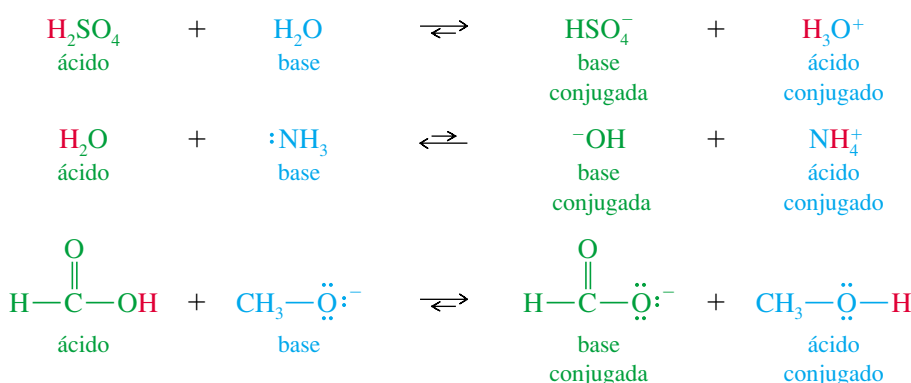
En 1923, Brønsted y Lowry definieron los ácidos y las bases teniendo en cuenta su capacidad de liberar o captar protones, respectivamente. Un **ácido de Brønsted-Lowry** es cualquier especie que puede donar un protón, y una **base de Brønsted-Lowry** es cualquier especie que puede aceptar un protón. Estas definiciones también incluyen todos los ácidos y bases de Arrhenius, ya que los compuestos que se disocian para dar H_3O^+ son donadores de protones y los compuestos que se disocian para dar OH^- son aceptores de protones (el ión hidróxido acepta un protón para formar H_2O).

Además de los ácidos y bases de Arrhenius, la definición de Brønsted-Lowry incluye también las bases que no tienen iones hidróxido, y que pueden aceptar protones. Observe los ejemplos siguientes de ácidos capaces de ceder protones a las bases. El NaOH es una base tanto si se considera la definición de Arrhenius o la de Brønsted-Lowry. Los tres ejemplos siguientes son bases de Brønsted-Lowry pero no bases de Arrhenius, ya que no tienen iones hidróxido.



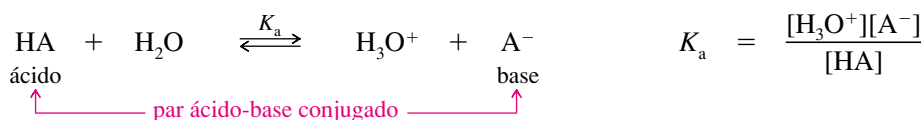


Cuando una base acepta un protón, se convierte en un ácido capaz de devolver ese protón. Cuando un ácido cede un protón, se convierte en una base capaz de aceptar de nuevo ese protón. Uno de los principios más importantes de la definición de Brønsted-Lowry es el concepto de **ácidos y bases conjugados**. Por ejemplo, el NH_3 y el NH_4^+ forman un par de ácido y base conjugados; el NH_3 es la base, cuando acepta un protón, se transforma en el ácido conjugado, NH_4^+ . Muchos compuestos (por ejemplo, el agua) pueden reaccionar como un ácido o como una base. A continuación se dan algunos ejemplos de pares ácido-base conjugados:



1.13A Fuerza de los ácidos

La fuerza de un ácido de Brønsted-Lowry se expresa de forma similar a la definición de Arrhenius, teniendo en cuenta su grado de ionización en agua. La reacción general de un ácido (HA) con agua es la siguiente:



A la K_a se la conoce con el nombre de *constante de disociación del ácido* y su valor indica la fuerza relativa del ácido. Cuanto más fuerte es el ácido, más se disocia, dando un valor de K_a mayor. Las constantes de disociación de un ácido varían en un intervalo amplio. Los ácidos fuertes se ionizan casi completamente en agua y sus constantes de disociación son superiores a 1. La mayoría de los ácidos orgánicos son ácidos débiles, con valores de K_a menores que 10^{-4} . Muchos compuestos orgánicos son ácidos extremadamente débiles; por ejemplo, el metano y el etano tienen un carácter ácido muy débil, su K_a es inferior a 10^{-40} .

Debido a este amplio margen de valores, las constantes de disociación ácida frecuentemente se expresan en escala logarítmica. El $\text{p}K_a$ de un ácido se define de forma parecida al pH: logaritmo (en base 10), con signo negativo, de la K_a .

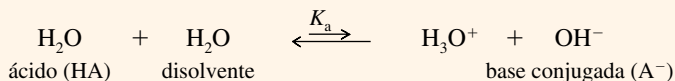
$$\text{p}K_a = -\log_{10} K_a$$

PROBLEMA RESUELTO 1.3

Calcule la K_a y el pK_a del agua.

SOLUCIÓN

El equilibrio que define la K_a del agua es:



El agua se comporta en esta disolución como ácido y como disolvente. La expresión del equilibrio es:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Donde $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$, constante del producto de ionización del agua.

La concentración de moléculas de H_2O en el agua simplemente es el número de moles de agua en 1 L (aproximadamente 1 kg).

$$\frac{1000 \text{ g/L}}{18 \text{ g/mol}} = 55.6 \text{ mol/L}$$

Haciendo la sustitución:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{1.00 \times 10^{-14}}{55.6} = 1.8 \times 10^{-16} \text{ M}$$

El logaritmo de 1.8×10^{-16} es -15.7 , por lo que el pK_a del agua es 15.7.

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En la mayor parte de los casos, el pK_a de un ácido coincide con el valor del pH de un ácido disociado en un 50%. A un pH menor (más ácido), el ácido estará menos disociado; a un pH mayor (más básico), el ácido estará más disociado.

Los ácidos fuertes generalmente tienen valores de pK_a próximos a 0 y los ácidos débiles, como la mayoría de los ácidos orgánicos, tienen valores superiores a 4. *Los ácidos más débiles tienen valores de pK_a más elevados.* La Tabla 1.5 recoge los valores de K_a y pK_a de algunos de los compuestos inorgánicos y orgánicos más habituales. Observa que los valores de pK_a aumentan cuando los valores de K_a disminuyen.

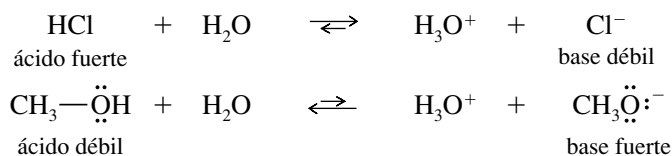
PROBLEMA 1.14

El amoníaco se encuentra en la Tabla 1.5 de dos formas, la forma básica y su ácido conjugado.

- Explique cómo el amoníaco puede actuar como base y como ácido. ¿Cuál de estas dos formas es más habitual en las soluciones acuosas?
- Explique por qué el agua puede actuar como ácido y como base.
- Explique por qué el metanol (CH_3OH) puede comportarse como ácido y como base. Escriba una ecuación para la reacción del metanol con el ácido sulfúrico.

1.13B Fuerza de las bases

La fuerza de un ácido es inversa a la fuerza de su base conjugada. Si un ácido (HA) es fuerte, su base conjugada (A^-) será débil, al ser estable en su forma aniónica; de lo contrario, el ácido HA no perdería fácilmente sus protones. Por lo tanto, la base conjugada de un ácido fuerte será una base débil. Por otra parte, si un ácido es débil, su conjugado es una base fuerte.

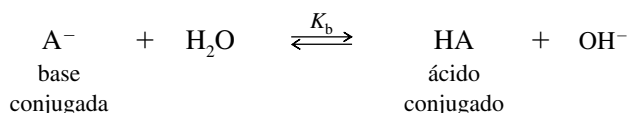


En la reacción de un ácido con una base, el equilibrio generalmente está desplazado hacia la formación de los ácidos y bases *débiles*. Por ejemplo, en las reacciones anteriores, el H_3O^+ es un ácido más débil que el HCl, pero un ácido más fuerte que el CH_3OH ; esto conlleva que el H_2O sea una base más fuerte que el Cl^- , pero más débil que el CH_3O^- .

TABLA 1.5 Fuerza relativa de algunos ácidos inorgánicos y orgánicos frecuentes, y sus bases conjugadas

	Ácido		Base conjugada	K_a	pK_a
ácidos fuertes	HCl ácido clorhídrico	$+ H_2O \rightleftharpoons H_3O^+ + Cl^-$	ion cloruro	1.6×10^2	-2.2
	HF ácido fluorhídrico	$+ H_2O \rightleftharpoons H_3O^+ + F^-$	ion fluoruro	6.8×10^{-4}	3.17
	$\begin{array}{c} O \\ \\ H-C-OH \end{array}$ ácido fórmico	$+ H_2O \rightleftharpoons H_3O^+ + \begin{array}{c} O \\ \\ H-C-O^- \end{array}$	ion formiato	1.7×10^{-4}	3.76
	$\begin{array}{c} O \\ \\ CH_3-C-OH \end{array}$ ácido acético	$+ H_2O \rightleftharpoons H_3O^+ + \begin{array}{c} O \\ \\ CH_3-C-O^- \end{array}$	acetano ion	1.8×10^{-5}	4.74
ácidos débiles	$H-C \equiv N:$ ácido cianhídrico	$+ H_2O \rightleftharpoons H_3O^+ + :C \equiv N:$	ion cianuro	6.0×10^{-10}	9.22
	$^+NH_4$ ion amonio	$+ H_2O \rightleftharpoons H_3O^+ + :NH_3$	amoniaco	5.8×10^{-10}	9.24
	CH_3-OH alcohol metílico	$+ H_2O \rightleftharpoons H_3O^+ + CH_3O^-$	metóxido ion	3.2×10^{-16}	15.5
	H_2O agua	$+ H_2O \rightleftharpoons H_3O^+ + HO^-$	ion hidróxido	1.8×10^{-16}	15.7
muy débil	NH_3 amoniaco	$+ H_2O \rightleftharpoons H_3O^+ + :\ddot{N}H_2$	ion amiduro	10^{-33}	33
no ácido	CH_4 metano	$+ H_2O \rightleftharpoons H_3O^+ + :\ddot{C}H_3$	anión metilo	$<10^{-40}$	>40

La fuerza de una base se mide de forma similar a la de los ácidos, usando la constante de equilibrio de la reacción de hidrólisis:



La constante de equilibrio (K_b) para esta reacción se conoce con el nombre de *constante de disociación de la base* para la base A^- . Debido a que esta constante tiene un amplio rango de valores, frecuentemente se expresa en forma logarítmica. El pK_b se define como el logaritmo (en base 10), cambiado de signo, de la K_b .

$$K_b = \frac{[HA][OH^-]}{[A^-]} \quad pK_b = -\log_{10} K_b$$

Cuando se multiplica K_a por K_b , se puede apreciar cómo la acidez de un ácido está relacionada con la basicidad de su base conjugada:

Las propiedades ácido-base de muchos productos naturales son importantes de cara a su aislamiento, a su distribución en el cuerpo y a justificar sus efectos terapéuticos. Por ejemplo, la morfina (p. 2), que se aísla de las adormideras (opio), llega al cerebro como base libre, en la que el nitrógeno no está cargado. Sin embargo, son sus especies cargadas las que actúan como analgésicas.

$$(K_a)(K_b) = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

constante del producto de ionización del agua

$$(K_a)(K_b) = 10^{-14}$$

Aplicando logaritmos:

$$\text{p}K_a + \text{p}K_b = -\log 10^{-14} = 14$$

El producto de K_a por K_b siempre es igual a la constante del producto iónico del agua, 10^{-14} . Si el valor de K_a es grande, el valor de K_b será pequeño; es decir, cuanto más fuerte es un ácido, más débil es su base conjugada. De forma similar, un valor pequeño de K_a (ácido débil) implica un valor grande de K_b (base fuerte).

Cuanto más fuerte es un ácido, más débil es su base conjugada.

Cuanto más débil es un ácido, más fuerte es su base conjugada.

Las reacciones ácido-base favorecen la formación de ácidos más débiles y/o bases más débiles.

SUGERENCIA PARA RESOLVER PROBLEMAS

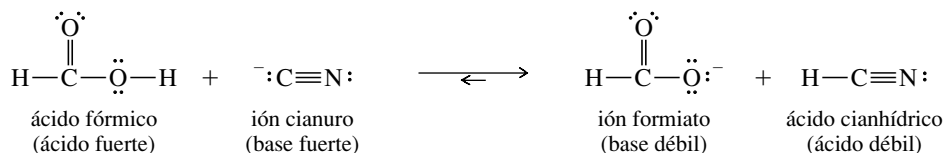
Un ácido donará un protón a la base conjugada de cualquier ácido que sea más débil (menor K_a o mayor $\text{p}K_a$).

PROBLEMA 1.15 (parcialmente resuelto)

Escriba las ecuaciones para las siguientes reacciones ácido-base. Utilice la información de la Tabla 1.5 para predecir si el equilibrio favorecerá a los reactivos o a los productos.

- | | |
|--|--|
| (a) $\text{HCOOH} + ^-\text{CN}$ | (b) $\text{CH}_3\text{COO}^- + \text{CH}_3\text{OH}$ |
| (c) $\text{CH}_3\text{OH} + \text{NaNH}_2$ | (d) $\text{NaOCH}_3 + \text{HCN}$ |
| (e) $\text{HCl} + \text{H}_2\text{O}$ | (f) $\text{H}_3\text{O}^+ + \text{CH}_3\text{O}^-$ |

Solución para (a): el ión cianuro es la base conjugada del HCN; puede aceptar un protón del ácido fórmico:



Observando la Tabla 1.5, se aprecia que el ácido fórmico ($\text{p}K_a = 3.76$) es un ácido más fuerte que el HCN ($\text{p}K_a = 9.22$) y que el cianuro es una base más fuerte que el formiato. Resultan favorecidos, pues, los productos ácido y base más débiles.

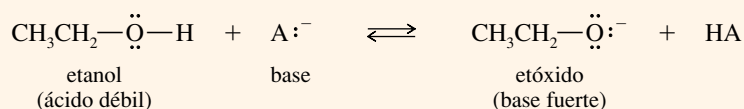
PROBLEMA RESUELTO 1.4

Cada uno de los compuestos siguientes puede actuar como un ácido. Escriba la reacción de cada compuesto con una base general (A^-) y la estructura de Lewis de la base conjugada que se obtiene.

- | | | |
|---------------------------------------|------------------------------|------------------------------|
| (a) $\text{CH}_3\text{CH}_2\text{OH}$ | (b) CH_3NH_2 | (c) CH_3COOH |
|---------------------------------------|------------------------------|------------------------------|

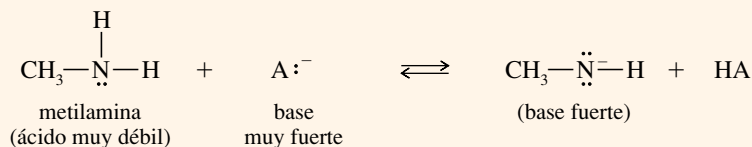
SOLUCIÓN

- (a) El etanol ($\text{CH}_3\text{CH}_2\text{OH}$) puede perder el protón del grupo $\text{O}-\text{H}$ para formar una base conjugada que es un ión orgánico análogo al ión hidroxilo.

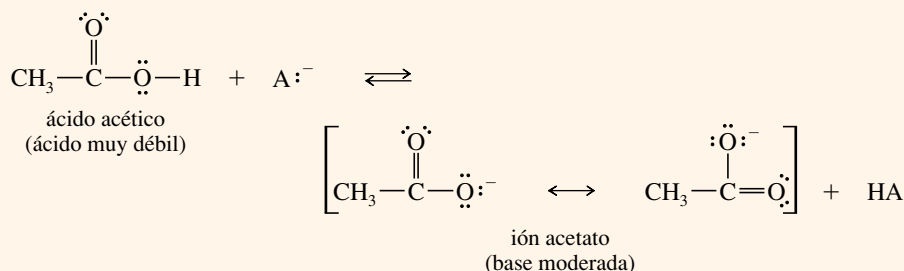


(Los protones del grupo $\text{C}-\text{H}$ son mucho menos ácidos que los protones del grupo $\text{O}-\text{H}$, porque el carbono es menos electronegativo que el oxígeno y, por lo tanto, la carga negativa es menos estable en el carbono.)

- (b) La metilamina (CH_3NH_2) es un ácido muy débil. Una base muy fuerte le puede sustraer un protón y dar lugar a una base conjugada fuerte.



- (c) El ácido acético (CH_3COOH) es un ácido moderadamente fuerte. Su base conjugada es el ión acetato que está estabilizado por resonancia.

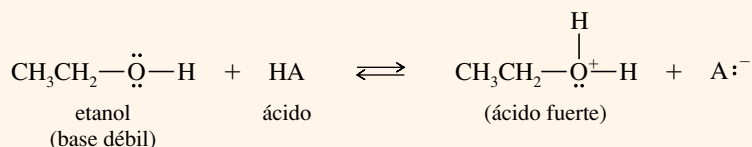


PROBLEMA RESUELTO 1.5

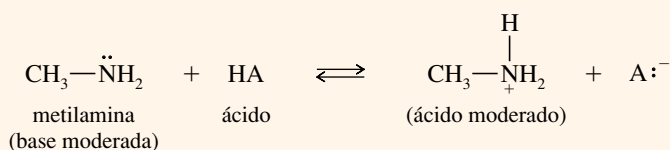
Cada uno de los compuestos del Problema resuelto 1.4 también pueden reaccionar como una base. Escriba la reacción de cada compuesto con un ácido general (HA) y las estructuras de Lewis del ácido conjugado que se obtiene.

SOLUCIÓN

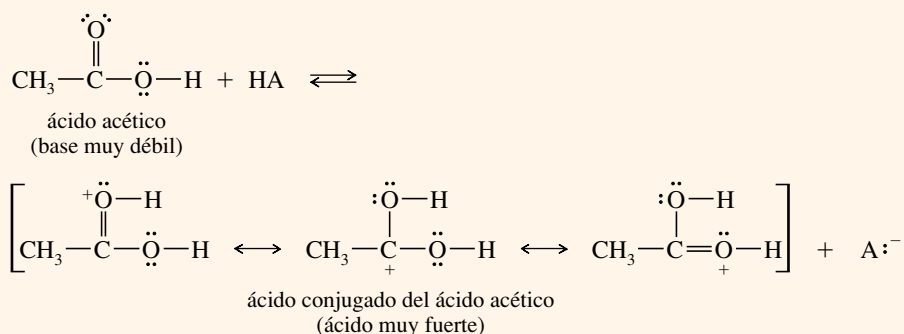
- (a) El etanol puede protonarse en su átomo de oxígeno. Observe que uno de los pares solitarios del oxígeno forma el nuevo enlace O—H.



- (b) El átomo de nitrógeno de la metilamina tiene un par de electrones que pueden enlazarse con un protón.



- (c) El ácido acético tiene electrones no enlazantes en los dos átomos de oxígeno. Cada uno de estos átomos de oxígeno podría protonarse, pero la protonación de oxígeno que forma parte del doble enlace está favorecida porque la protonación de este oxígeno da lugar a un ácido conjugado simétrico y estabilizado por resonancia.



PROBLEMA 1.16

El Problema resuelto 1.5(c) muestra la protonación del oxígeno con doble enlace del ácido acético. Escriba el producto obtenido de la protonación en el otro oxígeno (—OH). Explique por qué la protonación del oxígeno con doble enlace está favorecida.

PROBLEMA 1.17

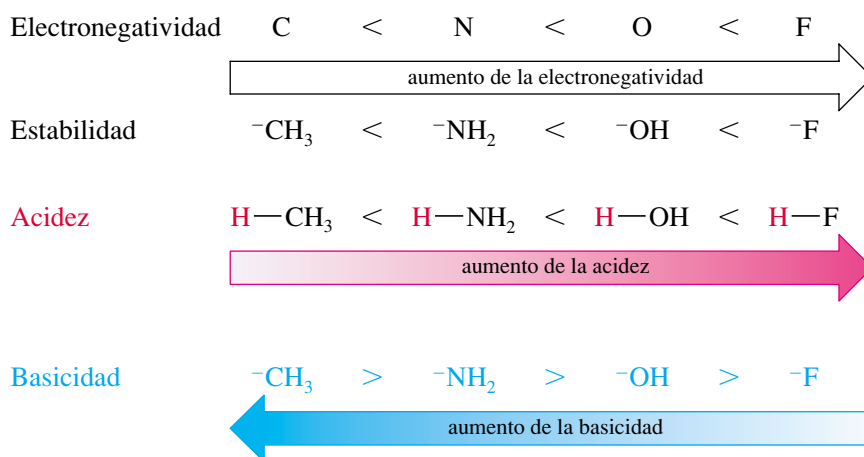
- (a) Ordene por orden decreciente de acidez el etanol, la metilamina y el ácido acético.
 (b) Ordene por orden decreciente de basicidad el etanol, la metilamina ($\text{p}K_b = 3.36$) y el ión etóxido ($\text{CH}_3\text{CH}_2\text{O}^-$). En cada caso, explique las razones de este orden.

1.13C Efectos estructurales en la acidez

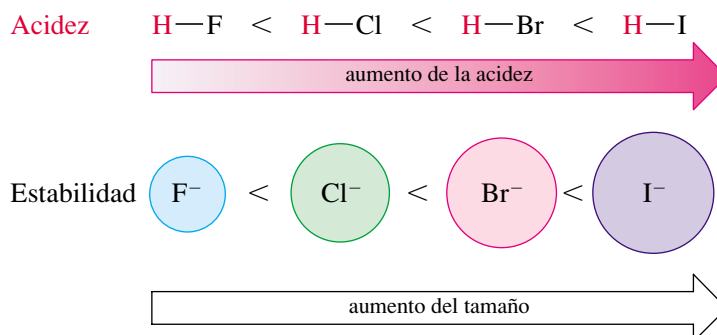
Cuando se observa una estructura, ¿cómo se puede predecir si el compuesto será un ácido fuerte o débil, o bien si no tendrá nada de carácter ácido? Según la teoría de Brønsted-Lowry, un ácido (HA) es un compuesto que ha de contener un átomo de hidrógeno que puede ser cedido como un protón. Un ácido fuerte debe formar una base conjugada estable (A^-) después de perder el protón.

La estabilidad de la base conjugada es una buena guía para conocer la fuerza del ácido. Los aniones más estables tienden a ser bases más débiles y sus ácidos conjugados tienden a ser ácidos más fuertes. Algunos de los factores que afectan a la estabilidad de las bases conjugadas son la electronegatividad, el tamaño y la resonancia.

Electronegatividad Cuanto más electronegativo sea un elemento, será capaz de adquirir una carga negativa con más facilidad, lo que dará lugar a una base conjugada más estable y a un ácido fuerte. La electronegatividad aumenta de izquierda a derecha en la tabla periódica.



Tamaño La carga negativa de un anión es más estable cuando se distribuye sobre una región del espacio más amplia. Si se considera una columna de la tabla periódica, la acidez aumenta hacia abajo, a medida que el tamaño de los elementos aumenta.



Estabilización por resonancia La carga negativa de una base conjugada puede estar deslocalizada entre dos o más átomos, y estabilizada por resonancia. Dependiendo de la electronegatividad que tengan esos átomos y de cómo se comparta esa carga, la deslocalización por resonancia con frecuencia es el efecto dominante que ayuda a la estabilización del anión. Observe las bases conjugadas siguientes:

Base conjugada	Ácido	pK _a
$\text{CH}_3\text{CH}_2-\ddot{\text{O}}:^-$ ión etóxido	$\text{CH}_3\text{CH}_2-\text{OH}$ etanol	15.9 (ácido débil)
$\left[\text{CH}_3-\overset{\text{O}}{\underset{\cdot\cdot}{\parallel}}\text{C}-\ddot{\text{O}}:^- \longleftrightarrow \text{CH}_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\parallel}}\text{C}=\ddot{\text{O}}:^- \right]$ ión acetato	$\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$ ácido acético	4.74 (ácido moderado)
$\left[\text{CH}_3-\overset{\text{O}}{\underset{\cdot\cdot}{\parallel}}\text{S}-\ddot{\text{O}}:^- \longleftrightarrow \text{CH}_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\parallel}}\text{S}=\ddot{\text{O}}:^- \longleftrightarrow \text{CH}_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\parallel}}\text{S}=\ddot{\text{O}}:^- \right]$ ión metanosulfonato	$\text{CH}_3-\overset{\text{O}}{\parallel}\text{S}-\text{OH}$ ácido metanosulfónico	-1.2 (ácido fuerte)

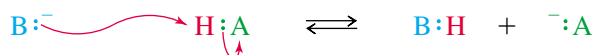
El ión etóxido es el más fuerte de las tres bases anteriores. El etóxido tiene una carga negativa localizada en un átomo de oxígeno; el ión acetato tiene una carga negativa compartida por dos átomos de oxígeno y el ión metanosulfonato tiene una carga negativa extendida sobre tres átomos de oxígeno. Los valores de los pK_a de los ácidos conjugados de esos aniones muestran que los ácidos son más fuertes si su desprotonación da lugar a bases conjugadas estabilizadas por resonancia.

PROBLEMA 1.18

Escriba las ecuaciones correspondientes a las reacciones ácido-base siguientes. Señale los ácidos y bases conjugados y justifique, si es el caso, su estabilización por resonancia escribiendo las posibles formas resonantes. Prediga si el equilibrio está desplazado hacia los reactivos o hacia los productos.

- (a) $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{NH}^-$ (b) $\text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{NHCH}_3$
 (c) $\text{CH}_3\text{OH} + \text{H}_2\text{SO}_4$ (d) $\text{NaOH} + \text{H}_2\text{S}$
 (e) $\text{CH}_3\text{NH}_3^+ + \text{CH}_3\text{O}^-$ (f) $\text{CH}_3\text{O}^- + \text{CH}_3\text{COOH}$
 (g) $\text{CH}_3\text{SO}_3^- + \text{CH}_3\text{COOH}$

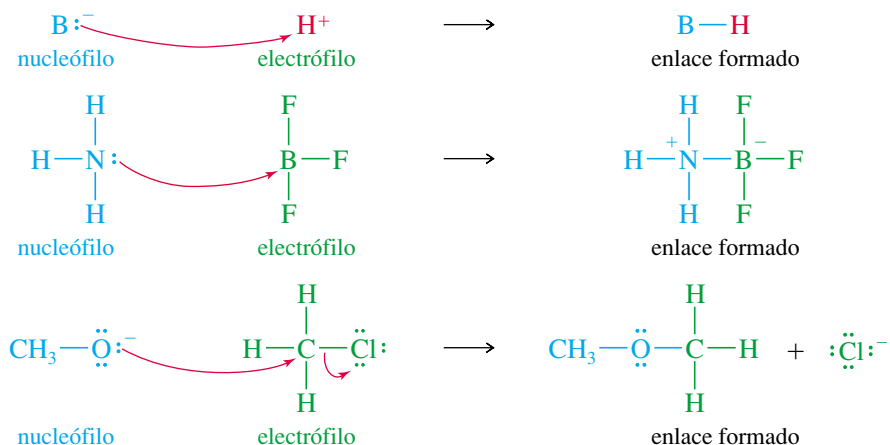
La definición de Brönsted-Lowry de ácidos y bases depende de la transferencia de un protón del ácido a la base. La base utiliza un par de electrones no enlazantes para formar un enlace con el protón. G. N. Lewis pensó que esta clase de reacciones no necesitaba obligatoriamente un protón para tener lugar. Una base podría usar su par solitario de electrones para enlazarse a algún otro átomo deficiente en electrones. En efecto, puede haber reacciones ácido-base desde el punto de vista de los *enlaces* que se forman y rompen, sin necesidad de que se transfiera un protón. La siguiente reacción muestra la transferencia del protón haciendo hincapié en los enlaces que se forman y que se rompen. Los químicos orgánicos utilizan de forma rutinaria flechas curvadas para mostrar el movimiento de los electrones que participan,



Las **bases de Lewis** son especies con electrones no enlazantes que pueden ser cedidos para formar nuevos enlaces. Los **ácidos de Lewis** son especies que pueden aceptar esos pares de electrones para formar nuevos enlaces. Debido a que un ácido de Lewis *acepta* un par de electrones, se le conoce como **electrófilo**, palabra derivada del griego, que significa «amante de electrones». A la base de Lewis se le llama **nucleófilo**, o «amante de los núcleos», ya que cede electrones a un núcleo que tenga un orbital vacío (o prácticamente vacío). En este libro, a veces se usan caracteres coloreados para enfatizar: azul para los nucleófilos, verde para los electrófilos y ocasionalmente rojo para los protones ácidos.

1.14 Ácidos y bases de Lewis

Las definiciones ácido-base de Lewis incluyen reacciones que no tienen ninguna relación con los protones. A continuación se muestran algunos ejemplos de reacciones ácido-base de Lewis. Observe que los ácidos y las bases de Brønsted-Lowry también están incluidos dentro de la definición de Lewis, siendo el protón un electrófilo. Las flechas curvadas (rojas) se usan para mostrar el movimiento de los electrones, generalmente desde el nucleófilo al electrófilo.

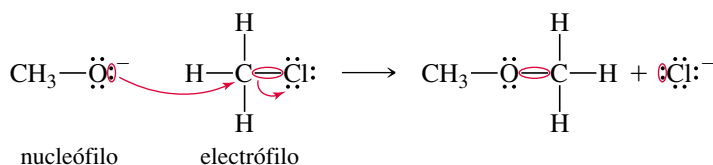


Algunos de los términos asociados con los ácidos y bases poseen significados específicos en química orgánica. Cuando un químico orgánico utiliza el término *base*, normalmente quiere decir «aceptor de protones» (una base de Brønsted-Lowry). De manera similar, el término *ácido* normalmente implica a un protón ácido (un ácido de Brønsted-Lowry). Cuando una reacción ácido-base implica la formación de un enlace con otro elemento (especialmente carbono), un químico orgánico denomina al donador de electrones *nucleófilo* (base de Lewis) y al aceptor de electrones, *electrófilo* (ácido de Lewis).

Las **flechas curvadas** se utilizan para mostrar el movimiento de un par de electrones *desde el donador de electrones al aceptor de electrones*. El movimiento de cada par de electrones implicado en formar o romper enlaces se indica por sus propias flechas separadas, como se muestra en las reacciones anteriores. En este libro, estas flechas curvadas se dibujan siempre en rojo. En la reacción anterior del CH_3O^- con CH_3Cl , una flecha curvada muestra el par solitario del oxígeno formando un enlace con el carbono; otra flecha curvada muestra que el par enlazante del $C-Cl$ se separa del átomo de carbono y se transforma en un par solitario formando el ión Cl^- .

SUGERENCIA PARA RESOLVER PROBLEMAS

Utilice una flecha curvada para cada par de electrones que participen en la reacción.



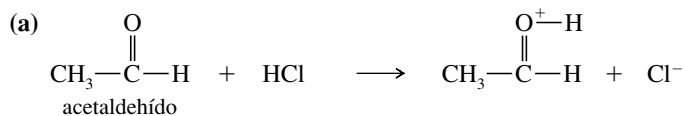
La flecha curvada se usa universalmente para seguir el camino del movimiento de los electrones en las reacciones; en este libro también se ha utilizado (en la Sección 1.9, por ejemplo) para seguir el movimiento de los electrones en las estructuras de resonancia, con objeto de representar el supuesto «flujo electrónico» cuando se pasaba de una estructura de resonancia a otra. Recuerde que los electrones no «fluyen» en las estructuras de resonancia, simplemente están deslocalizados. Este formalismo de las flechas nos ayuda, sin embargo, a comprender la interconversión entre las formas resonantes. Estas flechas curvadas se usan constantemente para seguir el camino de los electrones, tanto en el cambio de reactivos a productos como cuando imaginamos nuevas estructuras resonantes adicionales de un híbrido de resonancia.

PROBLEMA 1.19 (parcialmente resuelto)

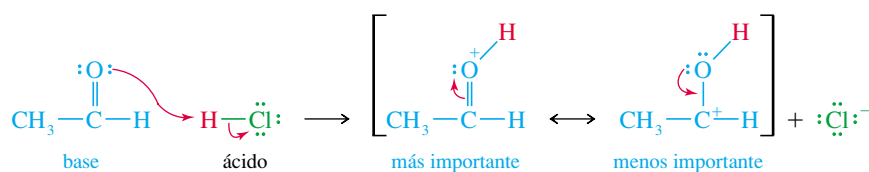
En las siguientes reacciones ácido-base:

- (1) Determine qué especies actúan como ácidos y cuáles como bases.
- (2) Utilice las flechas curvadas para mostrar el movimiento de los pares de electrones de las reacciones, así como el movimiento imaginario de electrones en los híbridos de resonancia de los productos.

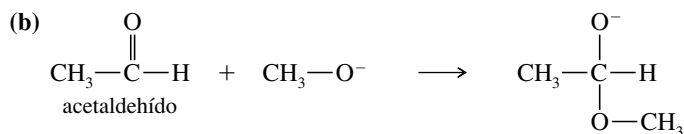
(3) Indique qué reacciones son las más apropiadas para poderlas incluir dentro de las reacciones ácido-base de Brønsted-Lowry.



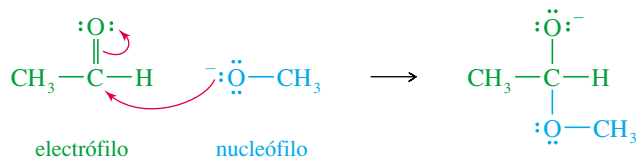
En esta reacción hay transferencia del protón del HCl al grupo C=O del acetaldehído, por tanto, es una reacción ácido-base de Brønsted-Lowry, donde el HCl actúa como ácido (donador de protones) y el acetaldehído actúa como base (aceptor de protones). Antes de dibujar una flecha curvada, recuerde que las flechas deben mostrar el movimiento de los electrones *desde* el donador del par de electrones (la base) *hasta* el aceptor del par de electrones (el ácido). Una flecha debe ir *desde* los electrones no enlazantes del acetaldehído *hasta* el átomo de hidrógeno del HCl y el enlace del ácido clorhídrico se ha de romper, con la formación del ión cloruro que ha captado los electrones del enlace H—Cl. Dibujar las flechas es fácil después de haber representado correctamente estructuras de Lewis de todos los reactivos y productos.



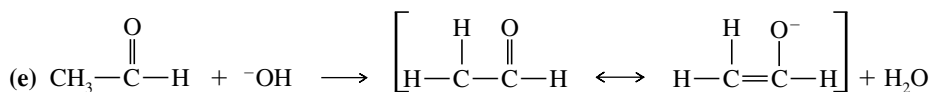
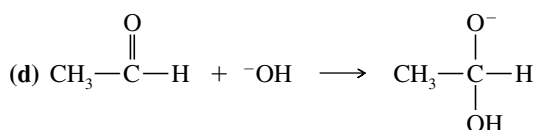
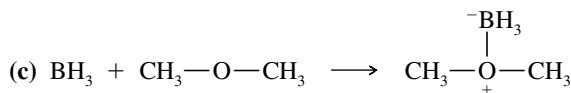
Las formas de resonancia del producto muestran que un par de electrones puede moverse entre el átomo de oxígeno y el enlace pi del C=O. La carga positiva está deslocalizada sobre los átomos de carbono y de oxígeno, con la mayor parte de la carga positiva sobre el oxígeno, ya que todos los octetos están completos en esa estructura de resonancia.



En este caso, ningún protón se ha transferido, por lo que no es una reacción ácido-base de Brønsted-Lowry. En su lugar, se ha formado un enlace entre el átomo de carbono del grupo C=O y el átomo de oxígeno del grupo CH₃—O[−]. Dibujar las estructuras de Lewis ayuda a ver que el grupo CH₃—O[−] (el nucleófilo en esta reacción) cede los electrones para formar el nuevo enlace con el acetaldehído (el electrófilo). Este resultado concuerda con la intuición de que un ión cargado negativamente es probablemente rico en electrones y por tanto un donador de electrones.



Observe que el acetaldehído actúa como nucleófilo (base) en (a) y como electrófilo en (b). Como la mayoría de los compuestos orgánicos, el acetaldehído puede ser tanto un ácido como una base. Actúa como una base si se le añade un ácido lo suficientemente fuerte para que ceda un par de electrones o capte un protón.



SUGERENCIA PARA RESOLVER PROBLEMAS

Las flechas curvadas se utilizan en los mecanismos para mostrar el *flujo de electrones* y no el movimiento de los átomos. Estas flechas curvadas se usarán constantemente a lo largo de este curso.

Glosario del Capítulo 1

Cada capítulo finaliza con un glosario que recoge los términos nuevos más importantes del capítulo. Estos glosarios son más que un diccionario en el que se buscan términos desconocidos conforme se los vaya encontrando (el índice sirve para este propósito). El glosario es una de las herramientas para revisar el capítulo, se puede leer cuidadosamente para saber si se entienden y se recuerdan todos los términos químicos mencionados. Cualquier concepto que no resulte familiar debería ser revisado volviendo a la página que aparece numerada en el mismo.

Ácido conjugado El ácido que resulta de la protonación de una base. (p. 23)

Ácido de Lewis, base de Lewis. Véase ácidos y bases.

Ácidos y bases (pp. 21-31)

(definiciones de Arrhenius)

Ácido: se disocia en agua para dar H_3O^+ .

Base: se disocia en agua para dar OH^- .

(definiciones de Brønsted-Lowry)

Ácido: donador de protones.

Base: aceptor de protones.

(definiciones de Lewis)

Ácido: aceptor de un par de electrones (electrófilo).

Base: donador de un par de electrones (nucleófilo).

Base conjugada La base que resulta de la pérdida de un protón de un ácido. (p. 23)

Cargas formales Método para hacer un seguimiento de las cargas, el cual permite mostrar qué carga habría en una determinada estructura de Lewis. (p. 11)

Densidad electrónica Probabilidad relativa de encontrar un electrón en una cierta región del espacio. (p. 3)

Electrófilo Aceptor de un par de electrones. (p. 29)

Electronegatividad Medida de la capacidad de un elemento para atraer electrones. Los elementos con electronegatividades más altas atraen a los electrones con más fuerza. (p. 10)

Electrones de valencia Electrones que se encuentran en la capa externa más alejada del núcleo. (p. 6)

Electrones no enlazantes Electrones de valencia que no se utilizan en el enlace. A un par de electrones no enlazantes con frecuencia se le denomina **par solitario**. (p. 7)

Enlace covalente Enlace que se forma por la compartición de electrones en la región que hay entre dos núcleos. (p. 7)

Enlace sencillo: enlace covalente en el que se comparte un par de electrones. (p. 8)

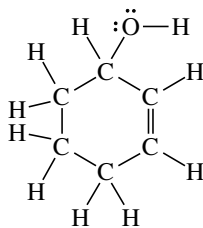
Enlace doble: enlace covalente en el que se comparte dos pares de electrones. (p. 8)

Enlace triple: enlace covalente en el que se comparte tres pares de electrones. (p. 8)

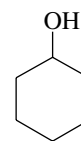
Enlace covalente polar Enlace covalente en el que los electrones se comparten de forma desigual. Cuando los electrones están igualmente compartidos se llama **enlace covalente no polar**. (p. 9)

Enlace iónico Enlace que se produce por la atracción de iones que tienen carga opuesta. El enlace iónico normalmente da lugar a la formación de una gran estructura cristalina en tres dimensiones. (p. 7)

Estructura de Lewis Fórmula estructural que muestra todos los electrones de valencia, con los enlaces simbolizados por líneas (—) o por pares de puntos, y los electrones no enlazantes simbolizados por puntos. (p. 7)



estructura de Lewis del 2-ciclohexenol



2-ciclohexenol
fórmula lineoangular equivalente

Flechas curvadas El dibujar flechas curvadas es un método que se utiliza para seguir el camino de los electrones cuando se mueven desde el nucleófilo al electrófilo (o dentro de una molécula) durante el transcurso de una reacción. (p. 30)

Fórmula empírica Relación numérica de los átomos en un compuesto. (p. 20). Véase también **fórmula molecular**.

Fórmula lineoangular (estructura esquelética o de barras) Fórmula estructural con enlaces representados por líneas; los átomos de carbono son los puntos de encuentro entre dos líneas o el final de la línea cuando está en el extremo de la cadena. Los átomos de nitrógeno, de oxígeno y los halógenos se representan, pero los átomos de hidrógeno no. Se supone que cada átomo de carbono tiene los hidrógenos suficientes para que en total tenga cuatro enlaces. (p. 19)

Fórmula molecular Número de átomos de cada elemento que forman parte de una molécula de un compuesto. La **fórmula empírica** simplemente da la relación de los átomos de los diferentes elementos. Por ejemplo, la fórmula molecular de la glucosa es $C_6H_{12}O_6$; su fórmula empírica es CH_2O . Ni la fórmula empírica ni la fórmula molecular dan información estructural. (p. 4)

Fórmulas estructurales Una **fórmula estructural completa** (tal como una estructura de Lewis) muestra todos los átomos y enlaces en la molécula. Una **fórmula estructural condensada** muestra cada átomo central y los átomos con los que está enlazado. Una **fórmula lineoangular** supone que hay un átomo de carbono donde dos líneas se encuentren, o donde la línea comience o termine. Véanse los ejemplos de la Sección 1.10. (p. 17)

Híbrido de resonancia Molécula o ión para el cual se pueden representar dos o más estructuras de Lewis válidas, diferenciándose solamente en la posición de los electrones de valencia. Estas estructuras de Lewis se conocen como **formas de resonancia** o **estructuras de resonancia**. Las formas de resonancia individuales no existen, pero se puede estimar sus energías relativas. A las estructuras más importantes (de energía más baja) se las conoce como **contribuyentes mayores**, y a las estructuras menos importantes (energía más alta), como **contribuyentes menores**. Cuando una carga se reparte entre dos o más átomos por resonancia, se dice que está **deslocalizada** y que la molécula está **estabilizada por resonancia**. (pp. 13-16)

Isótopos Átomos con el mismo número de protones pero diferente número de neutrones. Átomos del mismo elemento pero con diferentes masas atómicas. (p. 3)

Mapa de potencial electrostático (MPE) Representación molecular calculada por computador que utiliza colores para mostrar la distribución de carga en una molécula. En la mayoría de los casos, el MPE utiliza el color rojo para indicar las regiones ricas en electrones (potencial electrostático más negativo) y azul para indicar las regiones pobres en electrones (potencial electrostático más positivo). Los colores intermedios naranja, amarillo y verde indican regiones con potenciales electrostáticos intermedios. (p. 10)

Momento dipolar (μ) Medida de la polaridad de un enlace (o una molécula), proporcional al producto de la separación de cargas por la longitud de enlace. (p. 10)

Nodo Región de un orbital con densidad electrónica cero. (p. 4)

Nucleófilo Donador de par de electrones (base de Lewis). (p. 29)

Orbital Estado de energía permitida para un electrón que rodea a un núcleo; función de probabilidad que define la distribución de la densidad electrónica en el espacio. El *principio de exclusión de Pauli* afirma que un orbital sólo puede ser ocupado por dos electrones, como máximo, si los espines de éstos están apareados. (p. 3)

Orbitales degenerados Orbitales con energías idénticas. (p. 4)

Par solitario Par de electrones no enlazantes. (p. 7)

pH Medida de la acidez de una solución, definido como el logaritmo (en base 10), cambiado de signo, de la concentración de H_3O^+ . $pH = -\log_{10}[H_3O^+]$. (p. 22)

Plano nodal Región plana (plano) del espacio con densidad electrónica cero. (p. 4)

Química orgánica Definición nueva: química de los compuestos de carbono. Definición antigua: estudio de los compuestos derivados de los organismos vivos y sus productos naturales. (p. 1)

Regla de Hund Cuando hay dos orbitales o más con la misma energía (orbitales degenerados) vacíos, la configuración de energía más baja se consigue colocando los electrones en orbitales diferentes (con espines paralelos), mejor que colocándolos apareados en el mismo orbital. (p. 6)

Regla del octeto Los átomos generalmente se enlazan para que sus capas de valencia se completen con electrones (configuración de gas noble). Para los elementos de la segunda fila de la tabla periódica, esta configuración tiene ocho electrones de valencia. (p. 6)

Valencia Número de enlaces que normalmente forma un átomo. (p. 9)

Vitalismo Creencia en que la síntesis de compuestos orgánicos requiere la presencia de una «fuerza vital». (p. 1)

Pautas esenciales para resolver los problemas del Capítulo 1

1. Escribir e interpretar las fórmulas estructurales de Lewis, condensadas y lineoangulares. Indicar qué átomos tienen cargas formales.
2. Escribir formas de resonancia y usarlas para predecir la estabilidad.
3. Calcular fórmulas empíricas y moleculares de composiciones elementales.
4. Predecir la acidez y la basicidad relativa basada en la estructura, en el enlace y en la resonancia de los pares ácido-base conjugados.
5. Calcular, usar e interpretar los valores de K_a y pK_a .
6. Identificar nucleófilos (bases de Lewis) y electrófilos (ácidos de Lewis) y escribir ecuaciones de reacciones ácido-base de Lewis utilizando flechas curvadas para mostrar el flujo de los electrones.

Problemas

Es fácil engañarse a uno mismo pensando que se entiende la química orgánica cuando realmente no se entiende. Según se van leyendo a lo largo de este libro, todos los conceptos y las ideas pueden tener sentido, pero todavía no se ha aprendido a combinar y a usar esos conceptos e ideas. Un examen es un trance duro para darse cuenta de que realmente no se han entendido los contenidos.

La mejor forma de aprender química orgánica es aplicarla. Por supuesto se necesita leer y releer todo el material del capítulo, pero este nivel de entendimiento es justamente el comienzo. Se proponen problemas para poder trabajar con las ideas, aplicándolas a nuevos compuestos y reacciones que no se han visto con anterioridad. Al resolver problemas, uno se ve obligado a utilizar los conceptos y a entender lo que antes no se había comprendido, también se aumenta el nivel de autoestima y de habilidad para realizar los exámenes.

En cada capítulo se incluyen varias clases de problemas. Hay problemas dentro de los capítulos, que se introducen como ejemplos y explican cómo se han de resolver. Se ha de realizar ese tipo de problemas según se vaya leyendo el capítulo para asegurarse de que se han entendido los conceptos. Las soluciones de muchos de estos problemas se encuentran al final de libro. Los Problemas del final de cada capítulo proporcionan una experiencia adicional en el uso de los conceptos y obligan a pensar con detenimiento sobre las ideas expuestas en el texto. Para algunos de estos problemas se incluyen soluciones breves al final del libro, sin embargo, se pueden encontrar soluciones más detalladas de los mismos en el *Manual de Soluciones*.

Estudiar química orgánica sin resolver problemas es como lanzarse al aire sin paracaídas. Al principio parece divertido, pero después puede resultar duro para aquellos que carezcan de preparación.

1.20 Defina y ponga un ejemplo para cada término:

- | | | |
|------------------------------------|----------------------------|-------------------------------|
| (a) isótopos | (b) orbital | (c) nodo |
| (d) orbitales degenerados | (e) electrones de valencia | (f) enlace iónico |
| (g) enlace covalente | (h) estructura de Lewis | (i) electrones no enlazantes |
| (j) enlace sencillo | (k) enlace doble | (l) enlace triple |
| (m) enlace polar | (n) cargas formales | (o) formas de resonancia |
| (p) fórmula molecular | (q) fórmula empírica | (r) ácido y base de Arrhenius |
| (s) ácido y base de Brønsted-Lowry | (t) ácido y base de Lewis | (u) electrófilo |
| (v) nucleófilo | | |

1.21 Nombre el elemento que corresponda a cada configuración electrónica.

- (a) $1s^2 2s^2 2p^2$ (b) $1s^2 2s^2 2p^4$ (c) $1s^2 2s^2 2p^6 3s^2 3p^3$ (d) $1s^2 2s^2 2p^6 3s^2 3p^5$

1.22 Hay una pequeña sección de la tabla periódica que se debe conocer en química orgánica. Escriba de memoria esta parte, realizando los siguientes pasos:

- (a) Haga una lista, de memoria, de los elementos de las dos primeras filas de la tabla periódica, junto con su número de electrones de valencia.
 (b) Use esta lista para construir las dos primeras filas de la tabla periódica.
 (c) Los compuestos orgánicos a veces contienen azufre, fósforo, cloro, bromo y yodo. Añada estos elementos a la tabla periódica.

1.23 Para cada compuesto, diga si el enlace es covalente, iónico, o intermedio entre covalente e iónico.

- (a) NaCl (b) NaOH (c) CH_3Li (d) CH_2Cl_2 (e) NaOCH_3 (f) HCO_2Na (g) CF_4

1.24 (a) El PCl_3 y el PCl_5 son compuestos estables. Escriba la estructura de Lewis para los dos compuestos.

- (b) El NCl_3 es un compuesto conocido, pero todos los intentos de sintetizar el NCl_5 han fracasado. Escriba las estructuras de Lewis para el NCl_3 y una hipotética para el NCl_5 , y explique por qué el NCl_5 es una estructura improbable.

1.25 Escriba una estructura de Lewis para cada una de las especies.

- (a) N_2H_4 (b) N_2H_2 (c) $(\text{CH}_3)_4\text{NCl}$ (d) CH_3CN (e) CH_3CHO (f) $\text{CH}_3\text{S(O)CH}_3$
 (g) H_2SO_4 (h) CH_3NCO (i) $\text{CH}_3\text{OSO}_2\text{OCH}_3$ (j) $\text{CH}_3\text{C(NH)CH}_3$ (k) $(\text{CH}_3)_3\text{CNO}$

1.26 Escriba una estructura de Lewis para cada compuesto. Incluya todos los pares de electrones no enlazantes.

- (a) $\text{CH}_3\text{CHCHCH}_2\text{CHCHCOOH}$ (b) $\text{NCCH}_2\text{COCH}_2\text{CHO}$
 (c) $\text{CH}_2\text{CHCH(OH)CH}_2\text{CO}_2\text{H}$ (d) $\text{CH}_3\text{CH(CH}_3\text{)CH}_2\text{C(CH}_2\text{CH}_3\text{)}_2\text{CHO}$

1.27 Escriba la fórmula lineoangular de todos los compuestos del Problema 1.26.

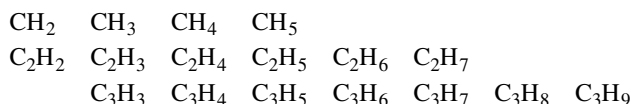
1.28 Escriba las estructuras de Lewis para:

- (a) dos compuestos de fórmula C_4H_{10} (b) dos compuestos de fórmula $\text{C}_2\text{H}_7\text{N}$
 (c) dos compuestos de fórmula $\text{C}_3\text{H}_8\text{O}_2$ (d) dos compuestos de fórmula $\text{C}_2\text{H}_4\text{O}$

1.29 Represente una fórmula estructural completa y una fórmula estructural condensada para:

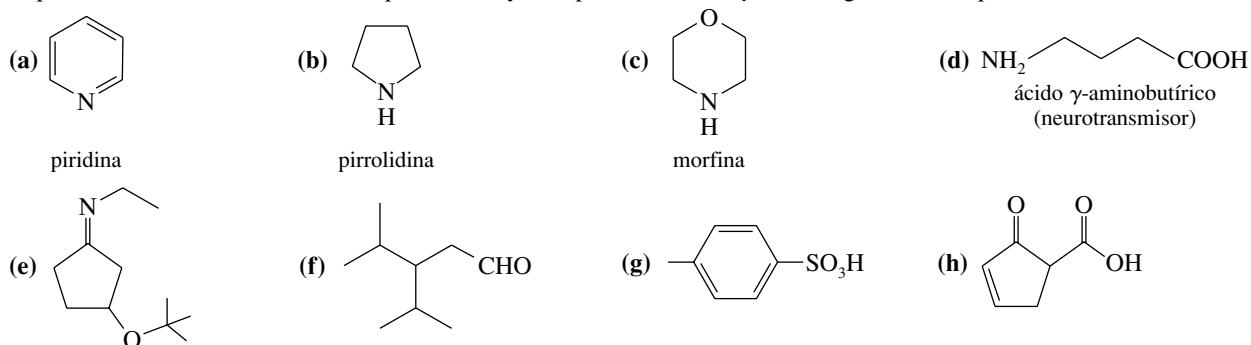
- (a) tres compuestos de fórmula $\text{C}_3\text{H}_8\text{O}$ (b) cinco compuestos de fórmula $\text{C}_3\text{H}_6\text{O}$

1.30 Alguna de las siguientes fórmulas moleculares corresponde a compuestos estables. Represente, cuando sea posible, una estructura estable para cada fórmula.



Proponga una regla general que dé el número de átomos de hidrógeno en los hidrocarburos estables.

1.31 Represente estructuras de Lewis completas, incluyendo pares solitarios, para los siguientes compuestos:



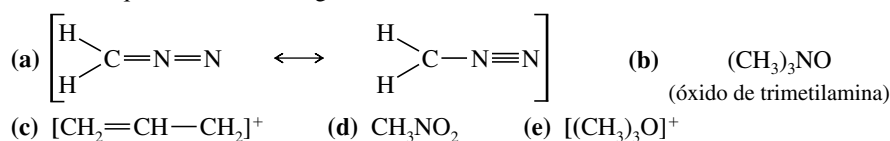
1.32 Escriba la fórmula molecular de todos los compuestos del Problema 1.31.

1.33 Un compuesto X, aislado de la lanolina (grasa de la lana de oveja), tiene un fuerte aroma a calcetines sucios sudados. Un análisis cuidadoso mostró que el compuesto X contenía un 62.0% de carbono y un 10.4% de hidrógeno. No se encontró nitrógeno ni halógenos.

- (a) Escriba la fórmula empírica del compuesto X.
 (b) La determinación del peso molecular mostró que el compuesto X tenía un peso molecular aproximadamente igual a 117; encuentre la fórmula molecular del compuesto X.
 (c) Hay muchas estructuras posibles que tienen esa fórmula molecular. Represente las fórmulas estructurales completas de cuatro de ellas.

1.34 Para cada una de las siguientes estructuras:

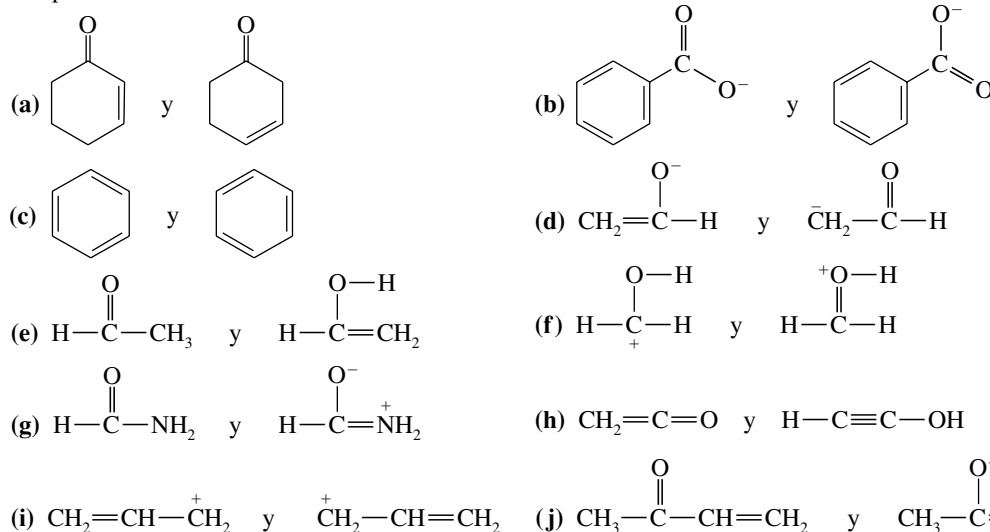
- (1) Represente una estructura de Lewis, poniendo también los electrones no enlazantes.
 (2) Calcule la carga formal de todos los átomos excepto del hidrógeno. Todos son eléctricamente neutros excepto aquellos en los que se indica su carga.



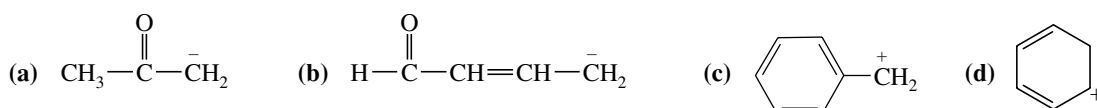
1.35 (1) Teniendo en cuenta la electronegatividad, establezca la dirección de los momentos dipolares de los siguientes enlaces.
 (2) En cada caso, prediga si el momento dipolar es relativamente grande o pequeño.

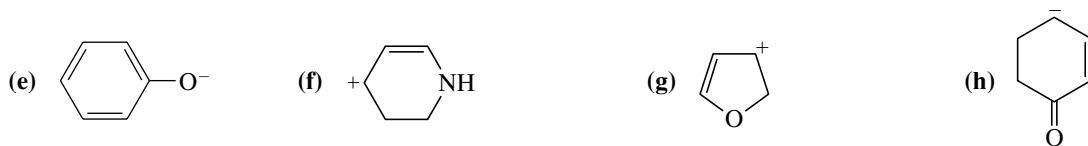
- (a) $\text{C}-\text{Cl}$ (b) $\text{C}-\text{H}$ (c) $\text{C}-\text{Li}$ (d) $\text{C}-\text{N}$ (e) $\text{C}-\text{O}$
 (f) $\text{C}-\text{B}$ (g) $\text{C}-\text{Mg}$ (h) $\text{N}-\text{H}$ (i) $\text{O}-\text{H}$ (j) $\text{C}-\text{Br}$

1.36 Determine si los siguientes pares de estructuras son diferentes compuestos o solamente formas de resonancia del mismo compuesto.



1.37 Represente las formas de resonancia importantes para mostrar la deslocalización de cargas en los iones siguientes:





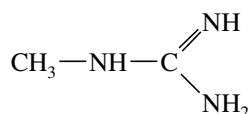
1.38

- (a) Represente las formas de resonancia para el SO_2 (conectividad $\text{O}-\text{S}-\text{O}$).
 (b) Represente las formas de resonancia para el ozono (conectividad $\text{O}-\text{O}-\text{O}$).
 (c) El dióxido de azufre tiene una forma de resonancia más que el ozono, explique por qué esa estructura no es posible para el ozono.

*1.39

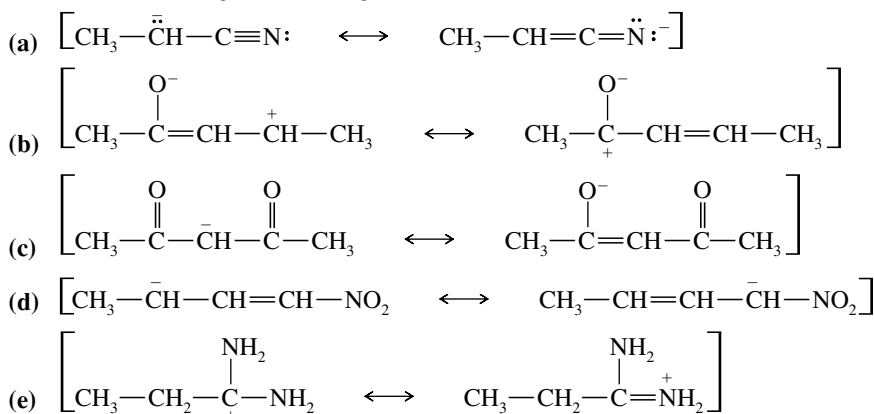
El compuesto siguiente puede protonarse en cualquiera de los átomos de nitrógeno, no obstante, uno de esos nitrógenos es mucho más básico que los otros.

- (a) Represente las formas de resonancia importantes de los productos de protonación de cada uno de los tres átomos de nitrógeno.
 (b) Determine qué átomo de nitrógeno es el más básico.



1.40

En los siguientes apartados de formas de resonancia, señale los contribuyentes mayor y menor, y diga qué estructuras tienen la misma energía. Si falta alguna forma de resonancia, añádala.



1.41

Para cada par de iones, determine cuál es más estable. Use formas de resonancia para explicar las respuestas.

- (a) $\text{CH}_3-\overset{+}{\text{CH}}-\text{CH}_3$ o $\text{CH}_3-\overset{+}{\text{CH}}-\text{OCH}_3$
 (b) $\text{CH}_2=\text{CH}-\overset{+}{\text{CH}}-\text{CH}_3$ o $\text{CH}_2=\text{CH}-\text{CH}_2-\overset{+}{\text{CH}}_2$
 (c) $\overset{-}{\text{CH}}_2-\text{CH}_3$ o $\overset{-}{\text{CH}}_2-\text{C}\equiv\text{N}:$



1.42

Ordene las siguientes especies por orden creciente de acidez, explicando las razones de este ordenamiento.



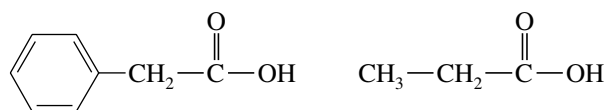
1.43

Ordene las siguientes especies por orden creciente de basicidad, explicando las razones de este ordenamiento.



1.44

La K_a del ácido fenilacético es 5.2×10^{-5} y el pK_a del ácido propiónico es 4.87.

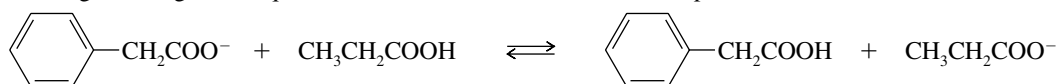


ácido fenilacético, $K_a = 5.2 \times 10^{-5}$ ácido propiónico, $pK_a = 4.87$

- (a) Calcule el pK_a del ácido fenilacético y la K_a del ácido propiónico.

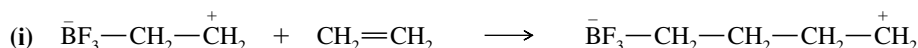
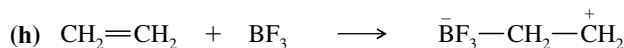
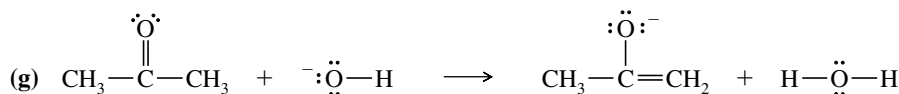
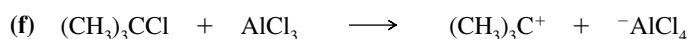
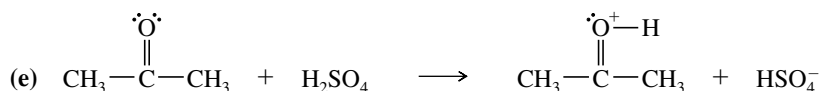
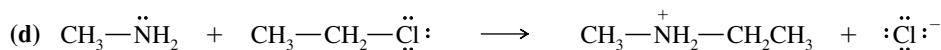
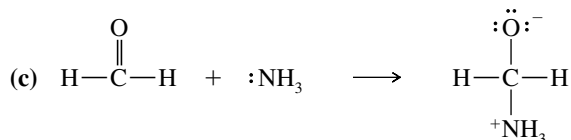
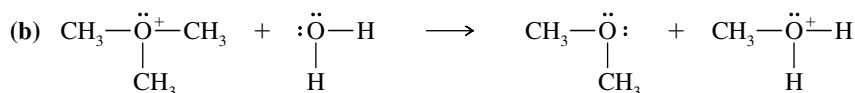
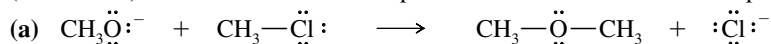
(b) ¿Cuál de los dos ácidos es el más fuerte? Calcule cuánto más fuerte es uno que otro.

(c) Prediga si el siguiente equilibrio favorecerá a los reactivos o a los productos.



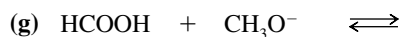
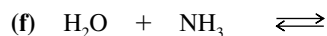
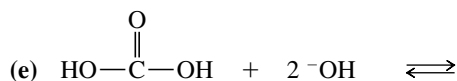
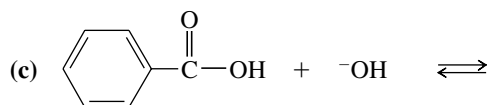
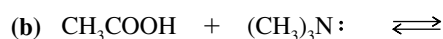
1.45

En las siguientes reacciones ácido-base clasifique los reactivos como ácidos de Lewis (electrófilos) o bases de Lewis (nucleófilos). Utilice flechas curvadas para indicar el movimiento de los pares de electrones en las reacciones.



1.46

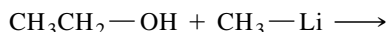
Prediga los productos de las siguientes reacciones ácido-base:



*1.47

El metilítio (CH_3Li) a menudo se usa como base en reacciones orgánicas.

(a) Prediga los productos de la siguiente reacción ácido-base:



(b) ¿Cuál es el ácido conjugado del CH_3Li ? ¿Qué es el CH_3Li ?, ¿una base fuerte o débil?

*1.48

En 1984, Edward A. Doisy de la Universidad de Washington extrajo 1 360 kg de ovarios de cerda para aislar unos pocos miligramos de estradiol puro, una potente hormona femenina. Doisy quemó 5.00 mg de esa preciada muestra en oxígeno y encontró que se obtenían 14.54 mg de CO_2 y 3.97 mg de H_2O .

(a) Determine la fórmula empírica del estradiol.

(b) La masa molecular del estradiol se determinó posteriormente y se encontró que era de 272. Determine la fórmula molecular del estradiol.

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2009

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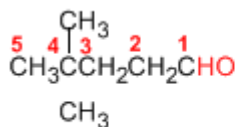
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- i. Nomenclatura de Aldehídos y Cetonas*
- ii. Preparación de Aldehídos y Cetonas*
- iii. Formación de Hidratos*
- iv. Formación de Hemiacetales*
- v. Formación de Acetales*
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- xviii. Problemas Resueltos de Aldehídos y Cetonas*
- xix. Teorías de Enoles y Enolatos*

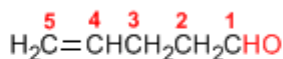
Nomenclatura de Aldehídos y Cetonas

Los aldehídos se nombran reemplazando la terminación **-ano** del alcano correspondiente por **-al**. No es necesario especificar la posición del grupo aldehído, puesto que ocupa el extremo de la cadena (localizador 1).

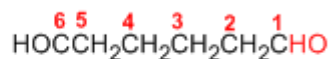
Cuando la cadena contiene dos funciones aldehído se emplea el sufijo **-dial**.



4,4-Dimetilpentanal

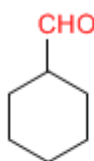


Hex-4-enal

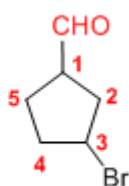


Pentanodial

El grupo **-CHO** unido a un ciclo se llama **-carbaldehído**. La numeración del ciclo se realiza dando localizador 1 al carbono del ciclo que contiene el grupo aldehído.



Ciclohexanocarbaldehído

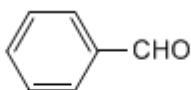


3-Bromociclopentanocarbaldehído

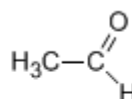
Algunos nombres comunes de aldehídos aceptados por la IUPAC son:



Formaldehído
(Metanal)

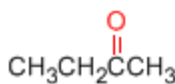


Benzaldehído
(Bencenocarbaldehído)

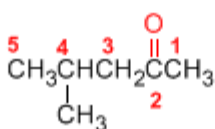


Acetaldehído
(Etanal)

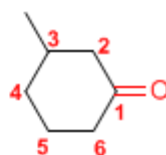
Las cetonas se nombran sustituyendo la terminación **-ano** del alcano con igual longitud de cadena por **-ona**. Se toma como cadena principal la de mayor longitud que contiene el grupo carbonilo y se numera para que éste tome el localizador más bajo.



Butanona

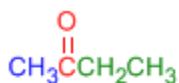


4-Metil-2-pentanona

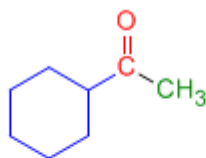


3-Metilciclohexanona

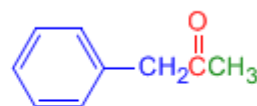
Existe un segundo tipo de nomenclatura para las cetonas, que consiste en nombrar las cadenas como sustituyentes, ordenándolas alfabéticamente y terminando el nombre con la palabra **cetona**.



Etil metil cetona



Ciclohexil metil cetona



Fenil metil cetona

[Siguiete >](#)

[\[Volver\]](#)

Charles Friedel (1832 - 1899)



Origen: Químico frances..

Lugar de nacimiento: Estrasburgo.

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

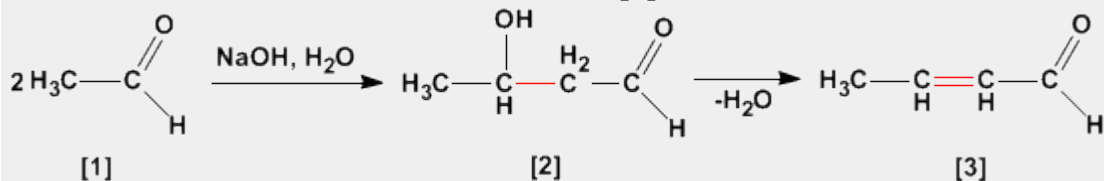
Docencia: Profesor en la Universidad de la Sorbona.

Investigación: Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

Premio Nobel:

Aldólica (Condensación)

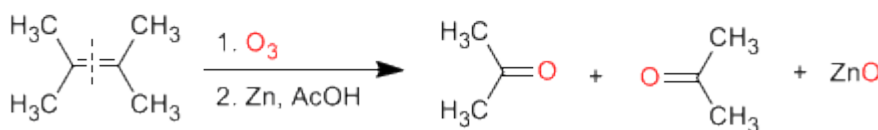
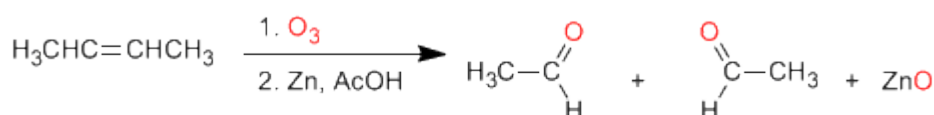
La condensación aldólica es una reacción de aldehídos o cetonas **[1]** que forma 3-hidroxicarbonilos (aldoles) **[2]**. El 3-hidroxialdehído **[2]** bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado **[3]**.



Preparación de aldehídos y cetonas

Los aldehídos y cetonas pueden ser preparados por oxidación de alcoholes, ozonólisis de alquenos, hidratación de alquinos y acilación de Friedel-Crafts como métodos de mayor importancia.

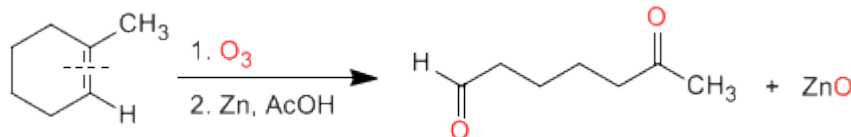
a) **Ozonólisis de alquenos:** Los alquenos rompen con ozono formando aldehídos y/o cetonas. Si el alqueno tiene hidrógenos vinílicos da aldehídos. Si tiene dos cadenas carbonadas forma cetonas.



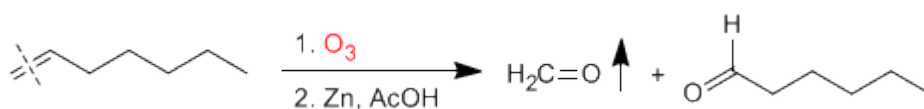
Ozonólisis

Los alquenos simétricos y terminales permiten la preparación de carbonilos mediante ozonólisis

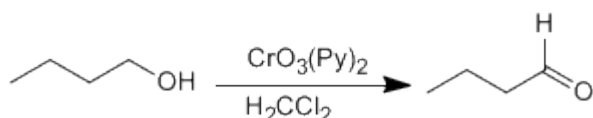
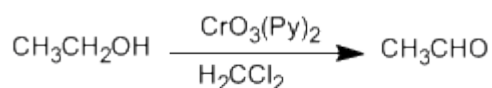
La ozonólisis de alquenos cíclicos produce compuestos dicarbonílicos:



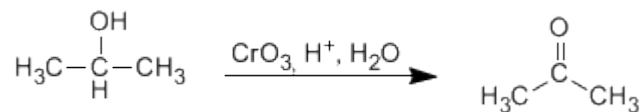
Los alquenos terminales rompen formando metanal, que separa fácilmente de la mezcla por su bajo punto de ebullición.



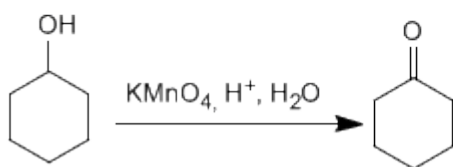
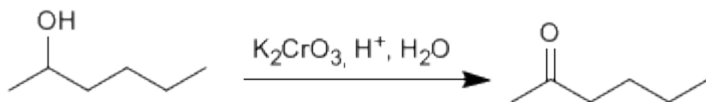
b) **Oxidación de alcoholes:** Los alcoholes primarios y secundarios se oxidan para dar aldehídos y cetonas respectivamente. Deben tomarse precauciones en la oxidación de alcoholes primarios, puesto que sobreoxidan a ácidos carboxílicos en presencia de oxidantes que contengan agua. En estos caso debe trabajarse con reactivos anhidros, como el clorocromato de piridino en diclorometano (PCC), a temperatura ambiente.



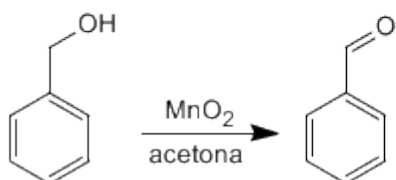
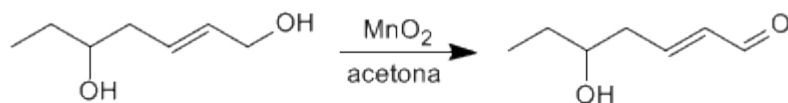
Los alcoholes secundarios dan cetonas por oxidación. Se emplean como oxidantes permanganato, dicromato, trióxido de cromo.



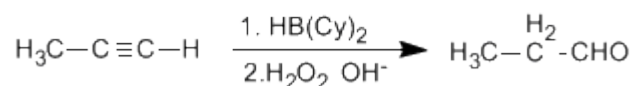
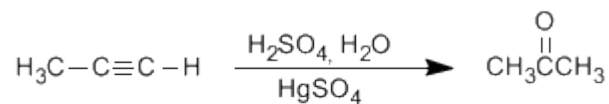
La oxidación supone la pérdida de dos hidrógenos del alcohol. Los alcoholes terciarios no pueden oxidar puesto que carecen de hidrógeno sobre el carbono.



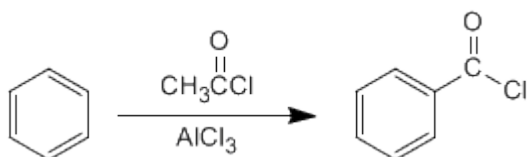
Los alcoholes alílicos y bencílicos se transforman en aldehídos o cetonas por oxidación con dióxido de manganeso en acetona. Esta reacción tiene una elevada selectividad y no oxida alcoholes que no se encuentren en dichas posiciones.



c) **Hidratación de alquinos:** Los alquinos se pueden hidratar Markovnikov, formando cetonas, o bien antiMarkovnikov, para formar aldehídos.



d) **Acilación de Friedel-Crafts:** La introducción de grupos acilo en el benceno permite la preparación de cetonas con cadenas aromáticas.



Otto Paul Hermann Diels (1876 - 1954)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

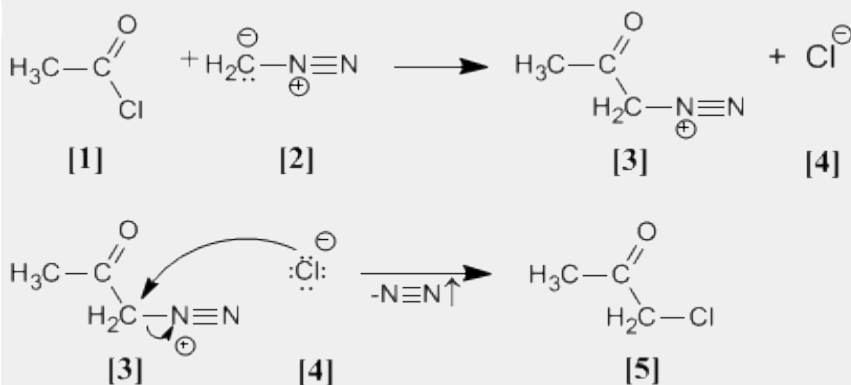
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Premio Nobel: En 1950 recibió el Premio Nobel junto a Kurt Alder

Arndt Eistert (Síntesis)

Cloruro de acetilo [1] se trata con diazometano [2] rindiendo la sal de diazonio [3]. El cloruro [4] producido reacciona con la sal de diazonio para dar la α -clorocetona [5].

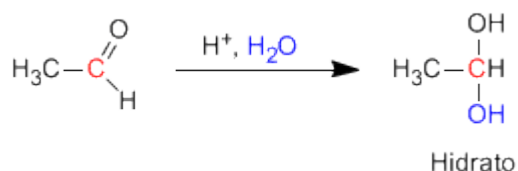


Síntesis de Arndt Eistert

Esta reacción permite transformar haluros de alcanoilo en cetonas halogenadas en su posición alfa.

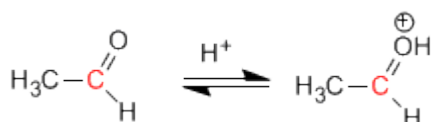
Formación de Hidratos

Los aldehídos y cetonas reaccionan en medio ácido acuoso para formar hidratos. El mecanismo consta de tres etapas. La primera y más rápida consiste en la protonación del oxígeno carbonílico. Esta protonación produce un aumento de la polaridad sobre el carbono y favorece el ataque del nucleófilo. En la segunda etapa el agua ataca al carbono carbonilo, es la etapa lenta del mecanismo. En la tercera etapa se produce la desprotonación del oxígeno formándose el hidrato final.

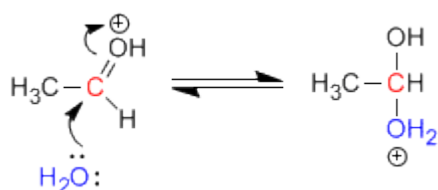


Mecanismo de la reacción

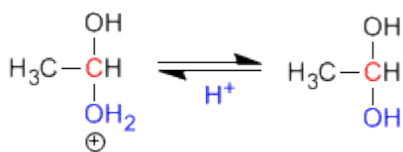
Etapa 1. Protonación del oxígeno carbonílico.



Etapa 2. Ataque nucleófilo del agua al carbonilo protonado.



Etapa 3. Desprotonación del hidrato





Origen: Químico estadounidense.

Lugar de nacimiento: Budapest

Formación: Se doctoró en la Universidad de Budapest en 1949

Docencia: Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

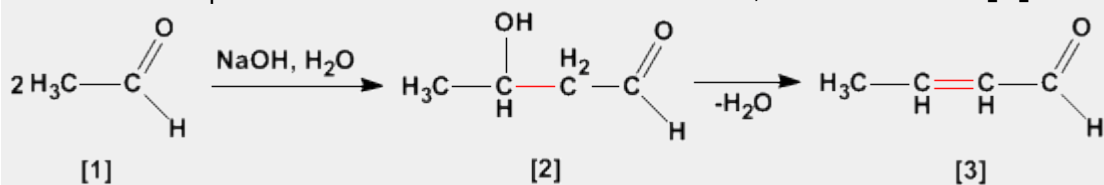
Industria: Trabajó en los laboratorios de la Dow Chemical de Ontario

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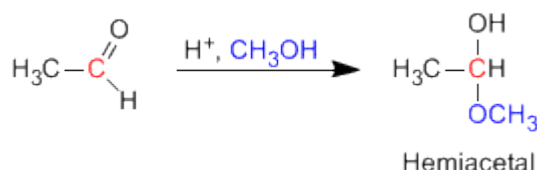
Aldólica (Condensación)

La condensación aldólica es una reacción de aldehídos o cetonas **[1]** que forma 3-hidroxicarbonilos (aldoles) **[2]**. El 3-hidroxialdehído **[2]** bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado **[3]**.



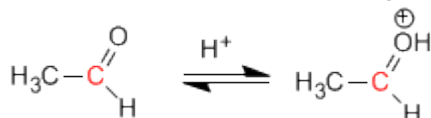
Formación de Hemiacetales

Los hemiacetales se forman por reacción de un equivalente de alcohol con el grupo carbonilo de un aldehído o cetona. Esta reacción se cataliza con ácido y es equivalente a la formación de hidratos.

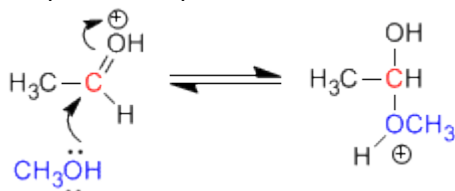


Mecanismo de la reacción:

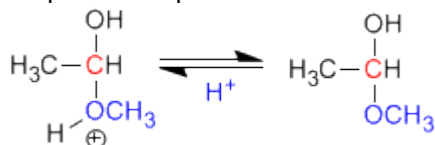
Eta 1. Protonación del oxígeno carbonílico.



Eta 2. Ataque nucleófilo del metanol al carbonilo protonado.



Eta 3. Desprotonación del hemiacetal



Otto Paul Hermann Diels (1876 - 1954)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

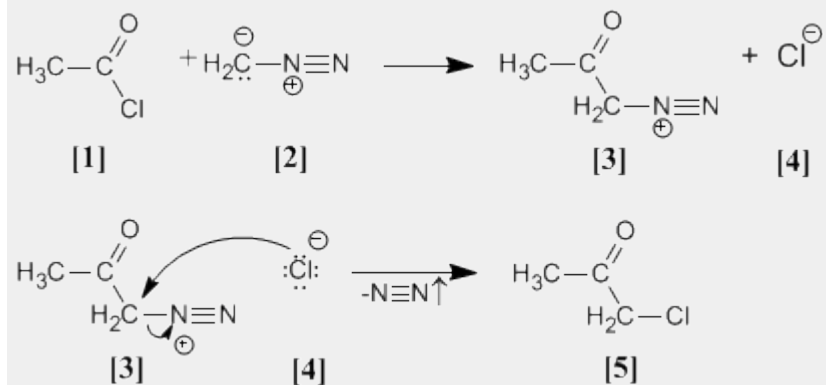
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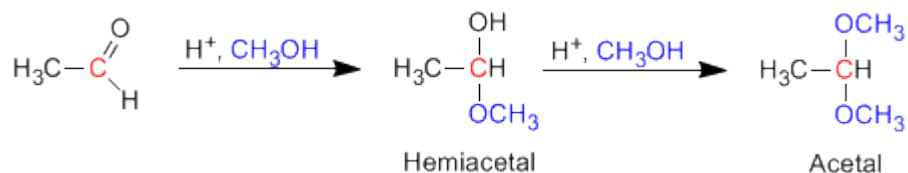
Arndt Eistert (Síntesis)

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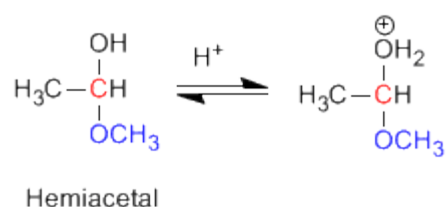
Formación de Acetales

Los aldehídos y cetonas reaccionan con alcoholes bajo condiciones de catálisis ácida, formando en una primera etapa hemiacetales, que posteriormene evolucionan por reacción con un segundo equivalente de alcohol a acetales.

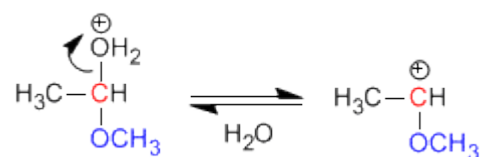


Mecanismo para la formación de acetales

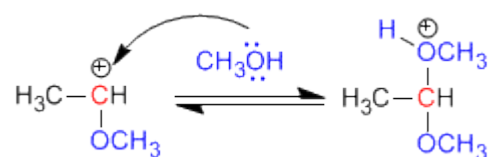
Etapa 1. Protonación del grupo hidroxilo



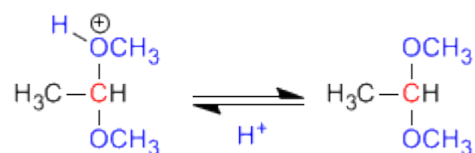
Etapa 2. Pérdida de agua.



Etapa 3. Ataque del alcohol al carbocatión



Etapa 4. Desprotonación del acetal



Otto Paul Hermann Diels (1876 - 1954)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

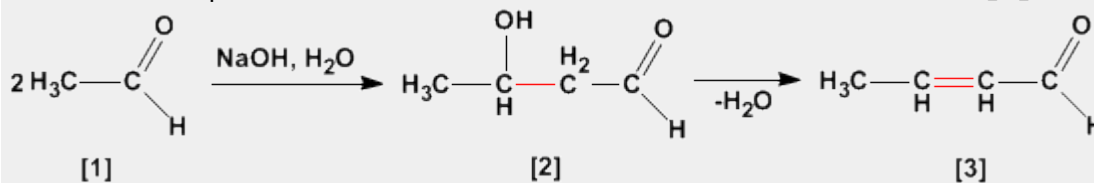
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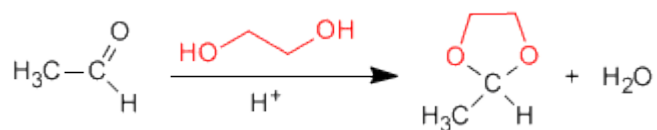
Aldólica (Condensación)

La condensación aldólica es una reacción de aldehídos o cetonas **[1]** que forma 3-hidroxicarbonilos (aldoles) **[2]**. El 3-hidroxialdehído **[2]** bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado **[3]**.



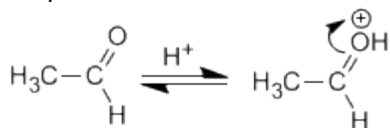
Formación de acetales cíclicos

Los 1,2- y 1,3-dioles reaccionan con aldehídos y cetonas formando acetales cíclicos. Los equilibrios se desplazan hacia el producto final eliminando el agua formada por destilación azeotrópica con benceno o tolueno.

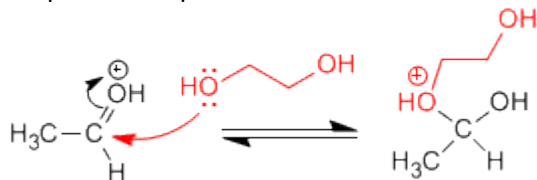


Mecanismo para la formación de acetales cíclicos:

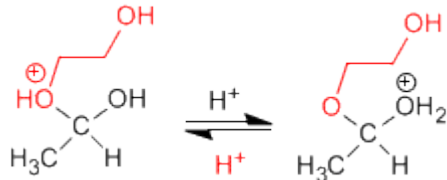
Etapa 1. Protonación del carbonilo



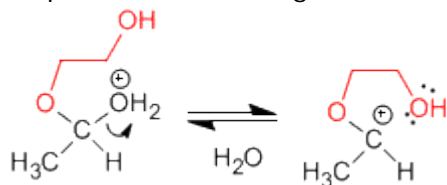
Etapa 2. Ataque nucleófilo del diol al carbonilo.



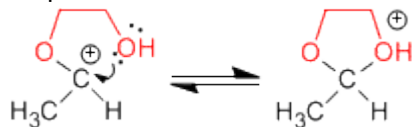
Etapa 3. Equilibrio ácido base entre el éter y el alcohol



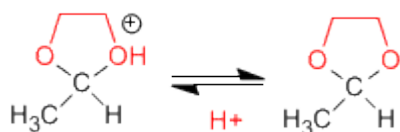
Etapa 4. Pérdida de agua



Etapa 5. Ciclación



Etapa 6. Desprotonación del acetal cíclico



Kurt Alder (1902 - 1958)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

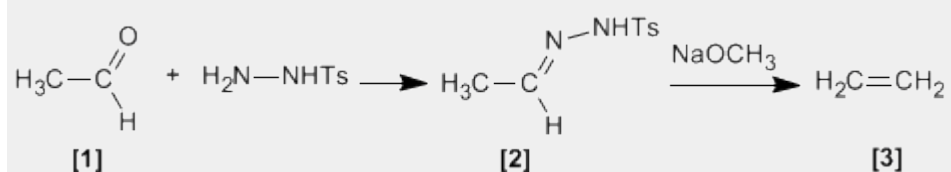
Docencia: Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

Investigación: Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos. Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

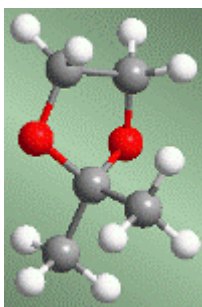
Premio Nobel: En 1950 recibió el Premio Nobel junto a Diels

Bamford Stevens (Reacción)

Tosilhidrazonas [2] de aldehídos o cetonas alifáticos [1] reaccionan con bases fuertes para dar alquenos [3].

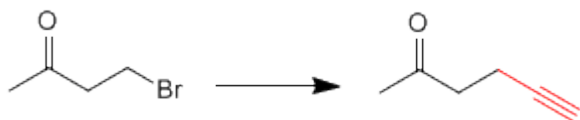


Acetales como grupos protectores

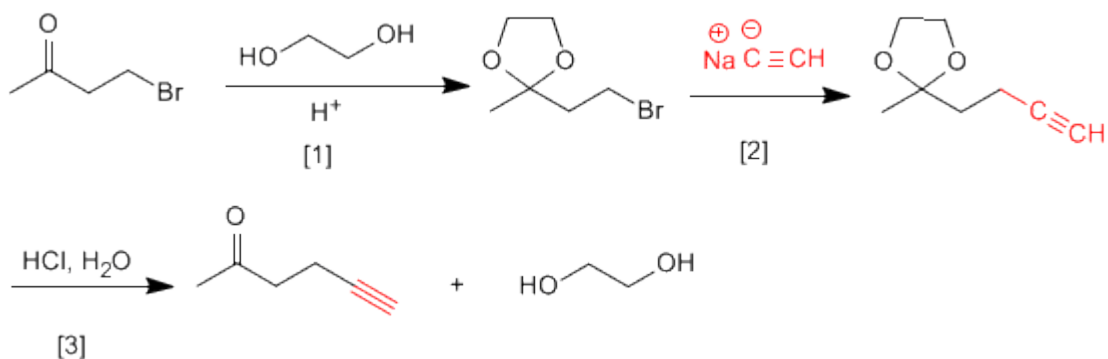


Los acetales pueden emplearse, por su estabilidad, como grupos protectores del carbonilo. El acetal es un éter, muy estable en medios básicos, aunque rompe en presencia de medios ácidos. En muchos procesos de síntesis el grupo carbonilo es incompatible con el reactivo utilizado. En estos casos debe protegerse para evitar que reaccione. La inestabilidad del acetal en medio ácido puede emplearse para desproteger el carbonilo.

Veamos algunos ejemplos:



Esta transformación requiere una sustitución, empleando como nucleófilo un acetiluro de sodio. El nucleófilo puede atacar también al grupo carbonilo, para evitarlo vamos a protegerlo.

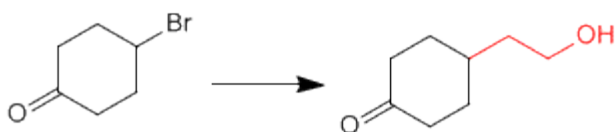


[1] Protección de la cetona.

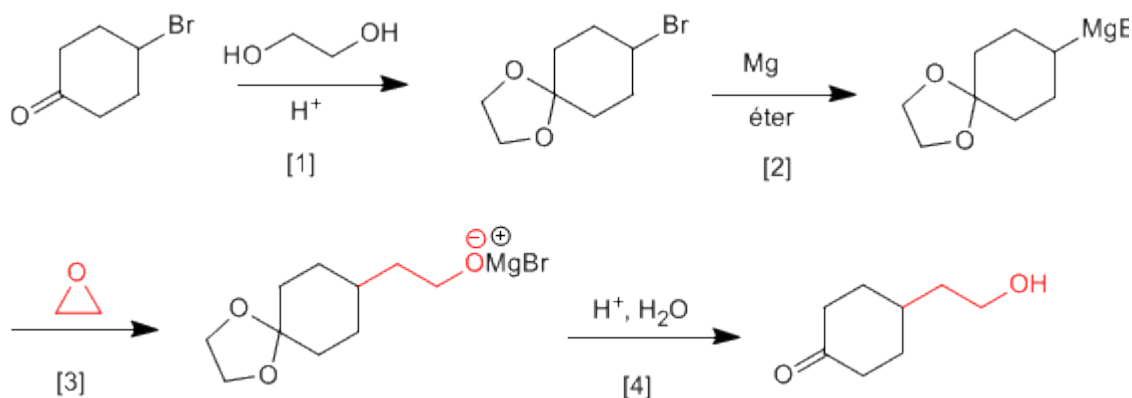
[2] Ataque del acetiluro al carbono del bromo.

[3] Desprotección del carbonilo

Veamos un segundo ejemplo:



Es necesario proteger la cetona antes de formar el organometálico para evitar la dimerización del compuesto.



- [1] Protección de la cetona.
 [2] Formación del magnesiano.
 [3] Apertura del oxaciclopropano.
 [4] Desprotección y protonación del alcóxido.

Otto Paul Hermann Diels (1876 - 1954)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

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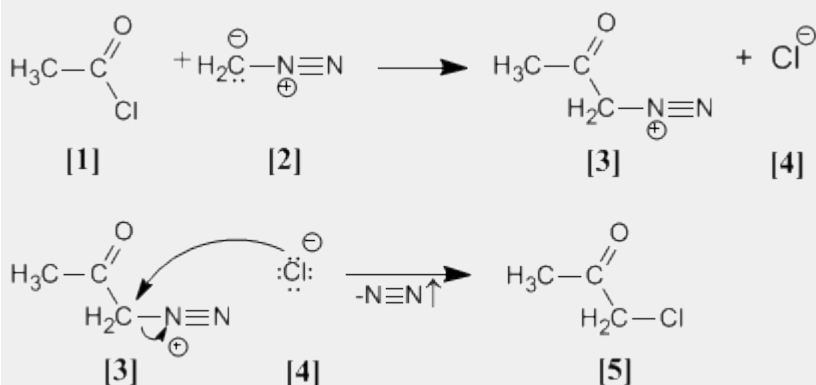
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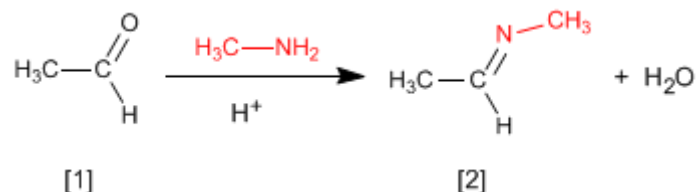
Arndt Eistert (Síntesis)

Cloruro de acetilo **[1]** se trata con diazometano **[2]** rindiendo la sal de diazonio **[3]**. El cloruro **[4]** producido reacciona con la sal de diazonio para dar la α-clorocetona **[5]**.



Formación de Iminas

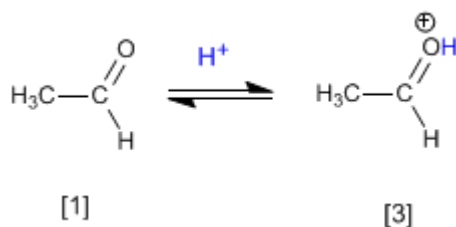
La reacción de aldehídos o cetonas **[1]** con aminas primarias genera iminas **[2]**. La reacción se favorece en un medio ligeramente ácido (pH=4.5).



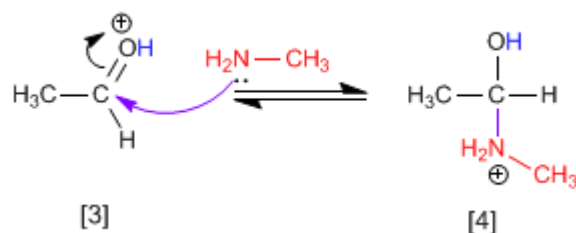
El control del pH es fundamental, puesto que se requiere la protonación del oxígeno del carbonilo para favorecer el ataque nucleófilo.

Mecanismo:

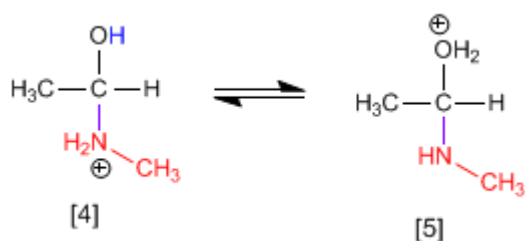
Etapla 1. Protonación del grupo carbonilo que aumenta la polaridad positiva sobre el carbono y favorece el ataque nucleófilo.



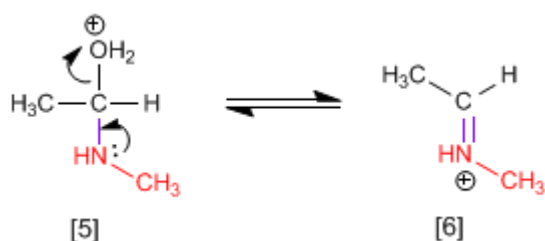
Etapla 2. Ataque nucleófilo de la amina primaria al carbono carbonilo.



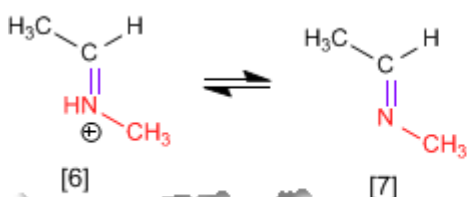
Etapla 3. Protonación del grupo hidroxilo para transformarlo en buen grupo saliente.



Etapla 4. Pérdida de agua y formación de la imina protonada.



Etapa 5. Desprotonación del catión.



George A. Olah (1927 -)



Origen: Químico estadounidense.

Lugar de nacimiento: Budapest

Formación: Se doctoró en la Universidad de Budapest en 1949

Docencia: Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

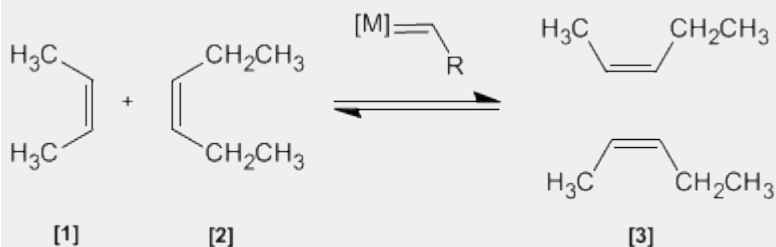
Industria: Trabajó en los laboratorios de la Dow Chemical de Ontario

Investigación: Olah consiguió preparar carbocationes estables utilizando componentes extremadamente ácidos.

Premio Nobel: En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

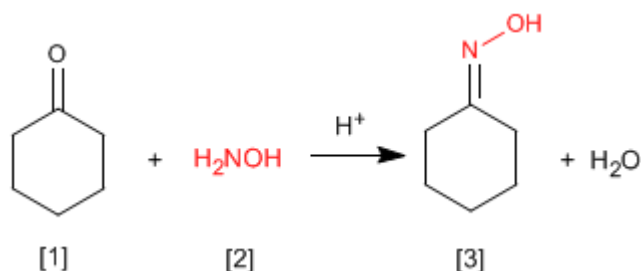
Metátesis de Alquenos

En esta reacción dos alquenos **[1]** y **[2]** son tratados con un metal de transición que actúa como catalizador, dando una mezcla de alquenos **[3]** (incluyendo isómeros Z/E). Este productos se obtiene por intercambio de grupos alquilideno.

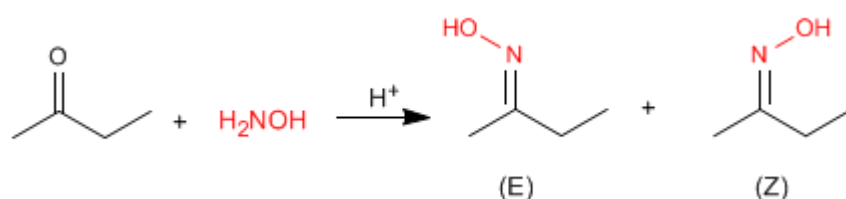


Formación de Oximas

Las oximas [3] se obtienen por reacción de aldehídos o cetonas [1] e hidroxilamina [2] en un medio débilmente ácido. El mecanismo es análogo al de formación de iminas.



Las oximas de aldehídos y cetona asimétricas presentan isomería Z/E dependiendo de la posición del hidroxilo.



Las iminas e hidrazonas (que comentaremos a continuación) también presentan esta característica.

George A. Olah (1927 -)



Origen: Químico estadounidense.

Lugar de nacimiento: Budapest

Formación: Se doctoró en la Universidad de Budapest en 1949

Docencia: Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

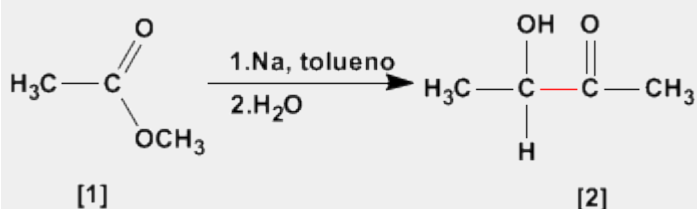
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Premio Nobel: En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

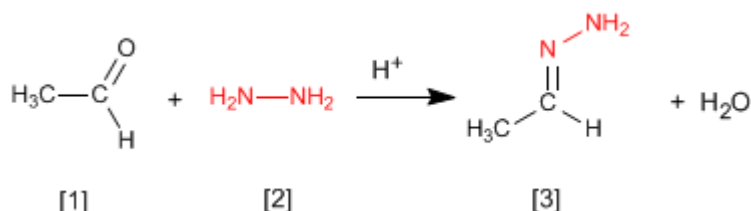
Aciloinica (Condensación)

La condensación aciloinica transforma ésteres [1] en alfa-hidroxicetonas [2]. Esta reacción se realiza con sodio metal en disolvente inerte.

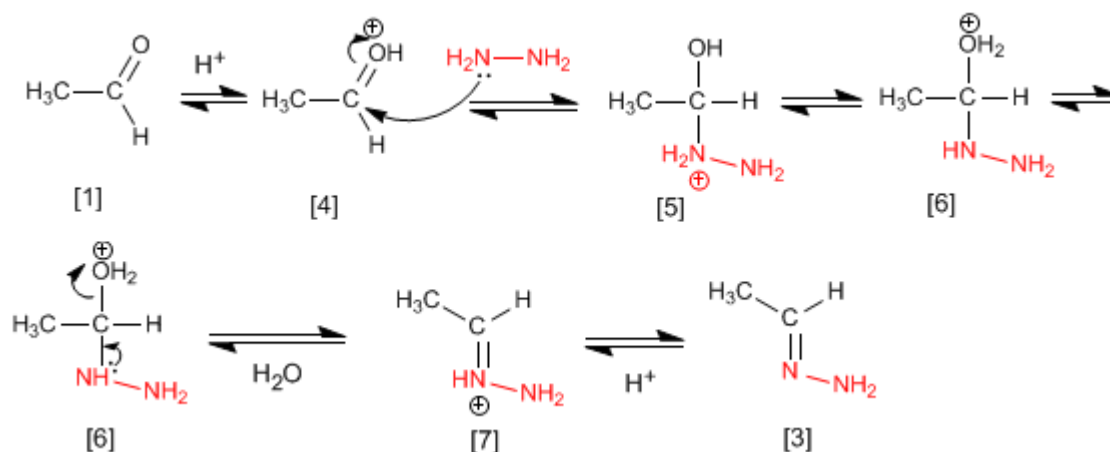


Formación de Hidrazonas

Las hidrazonas **[3]** se obtienen por reacción de aldehídos o cetonas **[1]** con hidrazina **[2]**. Igual que en el caso de las iminas y oximas requiere pH=4.



Aunque el mecanismo es análogo al de formación de iminas, comentaremos de nuevo los pasos.



El etanal **[1]** se protona formando su ácido conjugado **[4]**. La importante polaridad del carbono carbonilo de **[4]** favorece el ataque de la hidrazina **[2]** para formando el intermedio **[5]**. El compuesto **[5]** intercambia un protón entre el nitrógeno y el oxígeno, transformando el grupo hidroxilo en agua (buen grupo saliente). El intermedio **[6]** pierde una molécula de agua transformándose en **[7]**, cuya desprotonación da la hidrazona final **[3]**.

Kurt Alder (1902 - 1958)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

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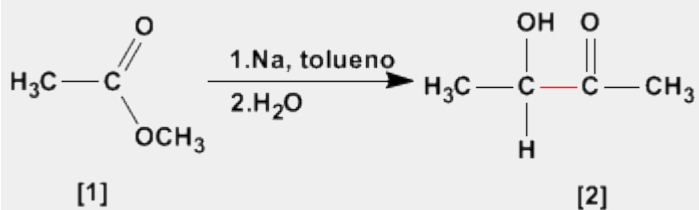
Investigación: Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos.

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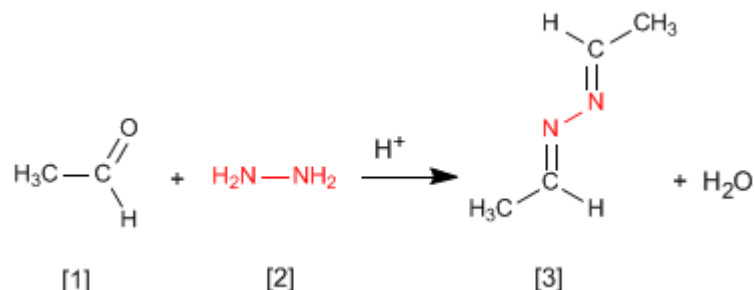
Aciloínica (Condensación)

La condensación aciloínica transforma esteres [1] en alfa-hidroxicetonas [2]. Esta reacción se realiza con sodio metal en disolvente inerte.



Formación de Azinas

La hidrazina [2] reacciona con dos moléculas de aldehído [1] para formar azinas [3].



El mecanismo es análogo al de formación de iminas, oximas e hidrazonas.

George A. Olah (1927 -)



Origen: Químico estadounidense.

Lugar de nacimiento: Budapest

Formación: Se doctoró en la Universidad de Budapest en 1949

Docencia: Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la

Universidad de Cleveland.

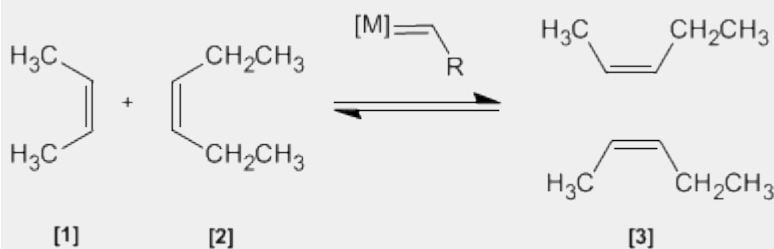
Industria: Trabajó en los laboratorios de la Dow Chemical de Ontario

Investigación: Olah consiguió preparar carbocationes estables utilizando componentes extremadamente ácidos.

Premio Nobel: En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

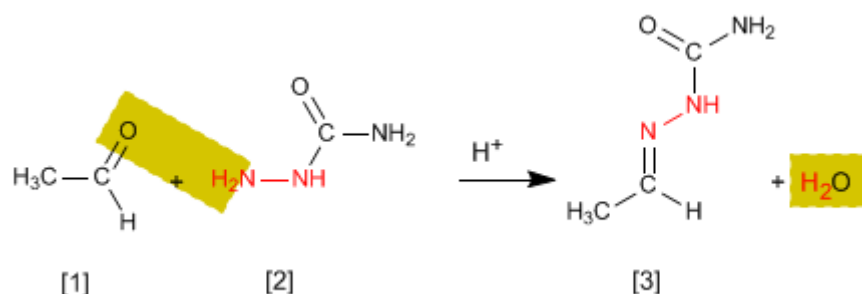
Metátesis de Alquenos

En esta reacción dos alquenos [1] y [2] son tratados con un metal de transición que actúa como catalizador, dando una mezcla de alquenos [3] (incluyendo isómeros Z/E). Este producto se obtiene por intercambio de grupos alquilideno.



Formación de Semicarbazonas

Las semicarbazonas [3] se obtienen por reacción de aldehídos o cetonas [1] con semicarbazida [2]. Veamos un ejemplo:



El mecanismo es análogo al de formación de iminas, oximas e hidrazonas.

Charles Friedel (1832 - 1899)



Origen: Químico frances..

Lugar de nacimiento: Estrasburgo.

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

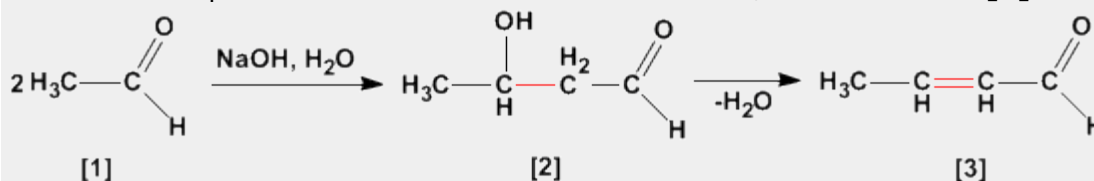
Docencia: Profesor en la Universidad de la Sorbona.

Investigación: Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

Premio Nobel:

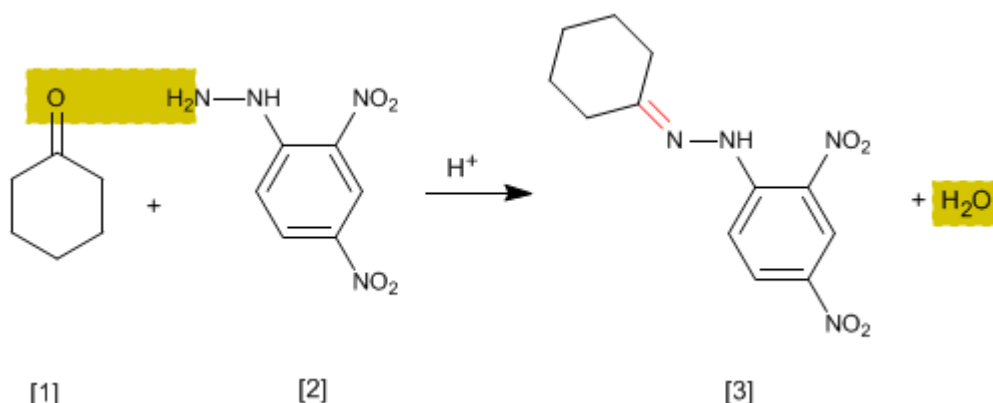
Aldólica (Condensación)

La condensación aldólica es una reacción de aldehídos o cetonas [1] que forma 3-hidroxicarbonilos (aldoles) [2]. El 3-hidroxialdehído [2] bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado [3].



Ensayo de la 2,4-Dinitrofenilhidrazina

Se trata de un ensayo analítico específico de aldehídos y cetonas. Los carbonilos **[1]** reaccionan con 2,4-Dinitrofenilhidrazina **[2]** formando fenilhidrazonas **[3]** que precipitan de color amarillo. La aparición de precipitado es un indicador de la presencia de carbonilos en el medio.



El mecanismo de la reacción es análogo al de formación de iminas.

Kurt Alder (1902 - 1958)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

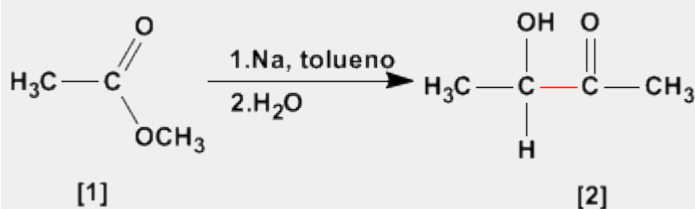
Docencia: Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

Investigación: Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos. Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

Premio Nobel: En 1950 recibió el Premio Nobel junto a Diels

Aciloinica (Condensación)

La condensación aciloinica transforma esteres **[1]** en alfa-hidroxicetonas **[2]**. Esta reacción se realiza con sodio metal en disolvente inerte.



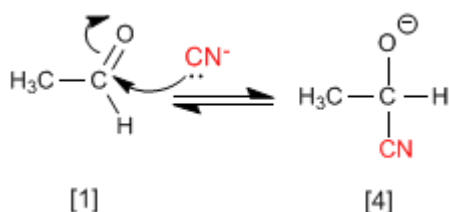
Formación de Cianhidrinas

Las cianhidrinas **[3]** se forman por reacción de aldehídos o cetonas **[1]** con ácido cianhídrico **[2]** y son compuestos que contienen un grupo ciano y un hidroxilo sobre el mismo carbono.

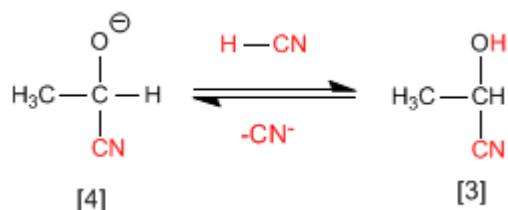


El mecanismo de la reacción transcurre en dos etapas:

Etapla 1. Los iones cianuro actúan como nucleófilos atacando al carbono carbonilo. El ácido cianhídrico es demasiado débil para generar cantidades importantes de cianuro, por ello, se añade cianuro de sodio o potasio al medio, garantizando la cantidad suficiente de cianuro para que la reacción transcurra en buen rendimiento.



Etapla 2. En este paso el ión alcóxido **[4]** se protona arrancando hidrógenos al ácido cianhídrico. En esta etapa se regeneran los iones cianuro.



Kurt Alder (1902 - 1958)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

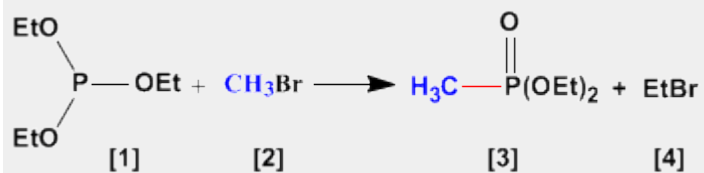
Docencia: Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

Investigación: Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos. Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

Premio Nobel: En 1950 recibió el Premio Nobel junto a Diels

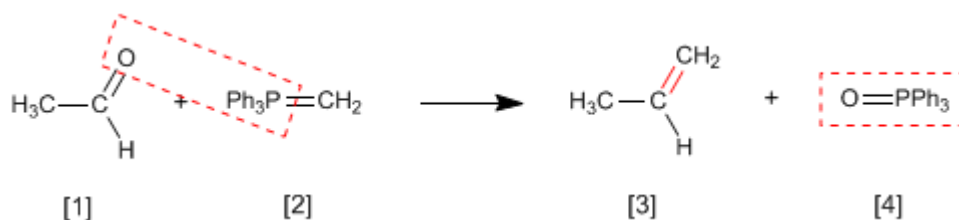
Arbuzov (Reacción)

La reacción de Arbuzov se emplea en la síntesis de fosfonatos **[3]** a partir de fosfitos **[1]**. Los fosfonatos obtenidos en la síntesis de Arbuzov se emplean como materiales de partida en la síntesis de Horner-Wittig.



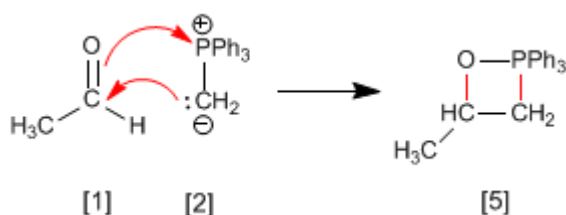
Reacción de Wittig

La reacción de Wittig emplea iluros de fósforo [2] para transformar aldehídos y cetonas [1] en alquenos [3]. Como subproducto se obtiene el óxido de trifenilfosfina [4].

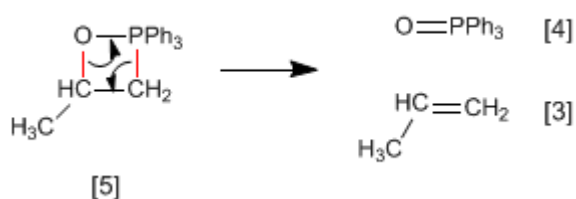


En el mecanismo de la reacción el iluro y el carbonilo se combinan para formar un oxafosfetano que rompe dejando libre el alqueno final.

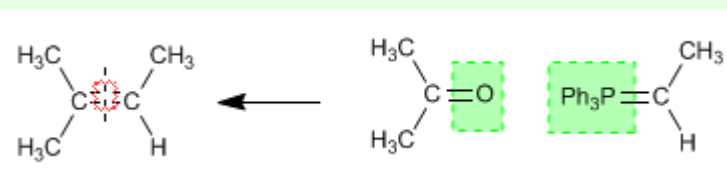
Etapas 1. El etanal y el iluro se combinan formando el fosfetano.



Etapas 2. El fosfetano rompe formando el alqueno y óxido de trifenilfosfina.



Ejemplo - Obtener mediante Wittig el 2-Metilbut-2-eno



Se rompe el alqueno por el doble enlace y a cada carbono se le agrega el grupo encerrado en verde.

Los **iluros de fósforo** se preparan mediante reacción de haloalcanos y trifenilfosfina, seguido de desprotonación del carbono con base fuerte (organometálicos de litio).



Charles Friedel (1832 - 1899)



Origen: Químico frances..

Lugar de nacimiento: Estrasburgo.

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

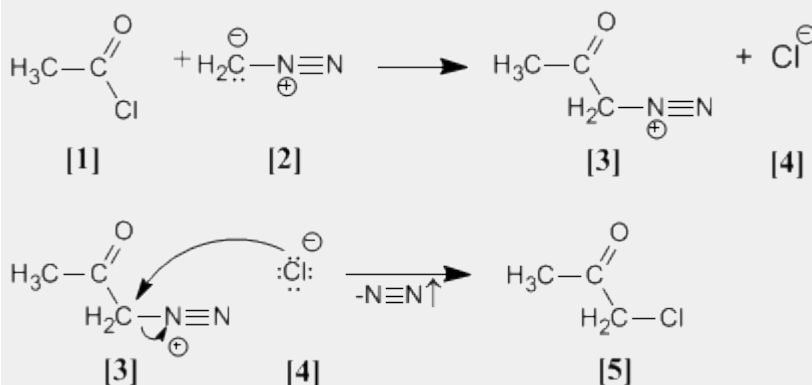
Docencia: Profesor en la Universidad de la Sorbona.

Investigación: Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

Premio Nobel:

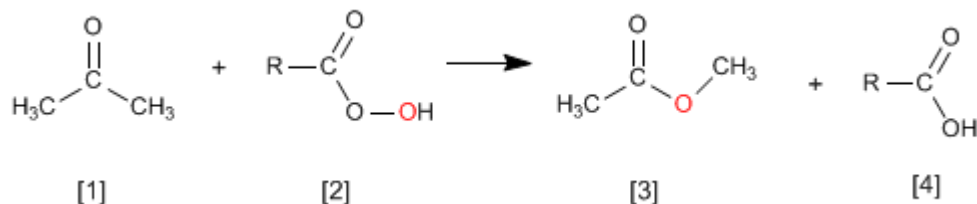
Arndt Eistert (Síntesis)

Cloruro de acetilo **[1]** se trata con diazometano **[2]** rindiendo la sal de diazonio **[3]**. El cloruro **[4]** producido reacciona con la sal de diazonio para dar la α-clorocetona **[5]**.

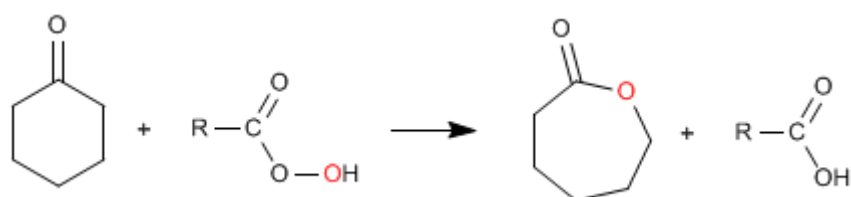


Oxidación de Baeyer Villiger

La reacción de cetonas **[1]** con perácidos **[2]** produce ésteres **[3]**. El oxígeno del perácido se inserta entre el carbono carbonilo y el carbono alfa de la cetona. Esta reacción fue descrita por Adolf von Baeyer y Victor Villiger in 1899.

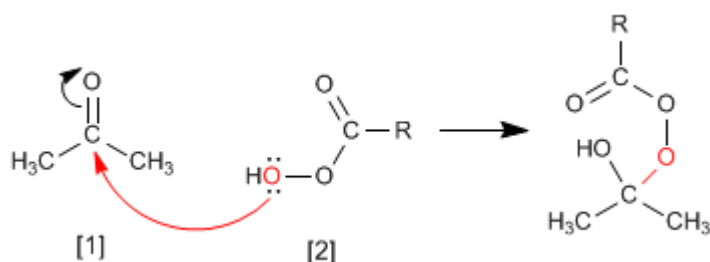


A partir de cetonas cíclicas se obtienen ésteres cíclicos (lactonas)

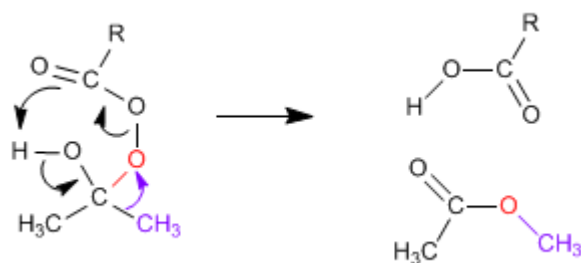


El mecanismo de Baeyer Villiger comienza con el ataque nucleófilo del perácido sobre el carbonilo, seguido de la migración del sustituyente desde el grupo carbonilo al oxígeno del perácido.

Etapas 1. Adición del perácido al carbonilo

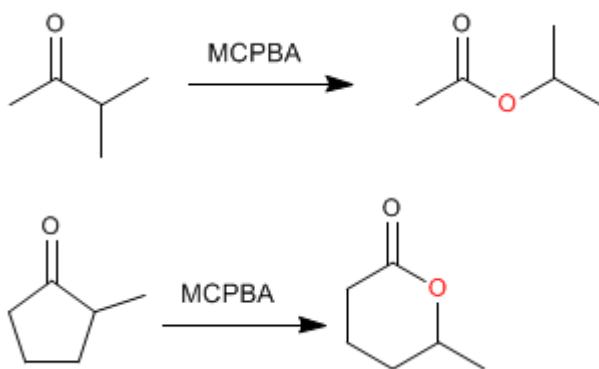


Etapas 2. Migración del sustituyente desde carbono carbonilo hacia el oxígeno (rojo)



Cuando la cetona tiene dos sustituyentes diferentes migra mejor el más sustituido. Existe un orden de migración que nos ayuda a decidir que sustituyente pasa a unirse al oxígeno del perácido.

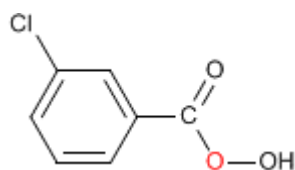
Orden de migración: H > carbono terciario > ciclohexilo > carbono secundario » fenilo > carbono primario > metilo



Como puede observarse en el orden de migración, el grupo que mejor migra, por su pequeño tamaño, es el hidrógeno, por ello, al tratar aldehídos con perácidos se produce la migración del hidrógeno formándose ácidos carboxílicos.



El **MCPBA** (Ácido meta-cloroperoxibenzoico) es un perácido ampliamente utilizado en la epoxidación de alquenos y también en Baeyer-Villger. La fórmula del MCPBA se muestra a continuación.



Charles Friedel (1832 - 1899)



Origen: Químico frances..

Lugar de nacimiento: Estrasburgo.

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

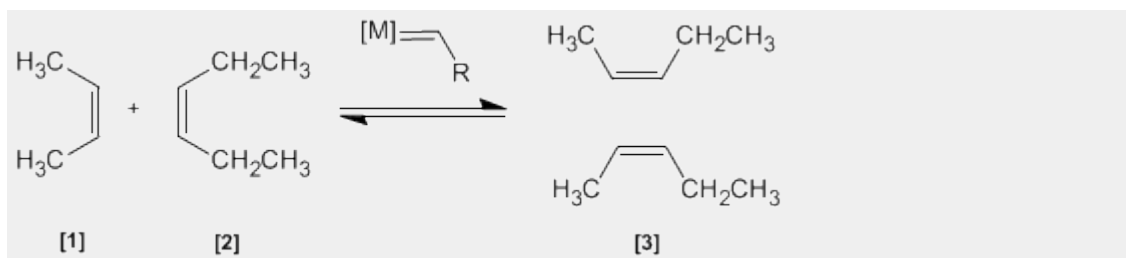
Docencia: Profesor en la Universidad de la Sorbona.

Investigación: Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

Premio Nobel:

Metátesis de Alquenos

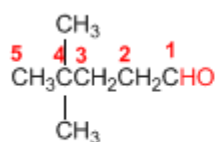
En esta reacción dos alquenos **[1]** y **[2]** son tratados con un metal de transición que actúa como catalizador, dando una mezcla de alquenos **[3]** (incluyendo isómeros Z/E). Este productos se obtiene por intercambio de grupos alquilideno.



Nomenclatura de Aldehídos y Cetonas - Reglas IUPAC

Regla 1. Los aldehídos se nombran reemplazando la terminación **-ano** del alcano correspondiente por **-al**. No es necesario especificar la posición del grupo aldehído, puesto que ocupa el extremo de la cadena (localizador 1).

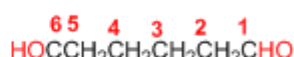
Cuando la cadena contiene dos funciones aldehído se emplea el sufijo **-dial**.



4,4-Dimetilpentanal

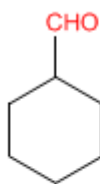


Hex-4-enal

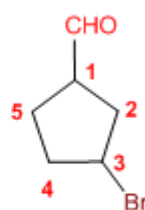


Hexanodial

Regla 2. El grupo **-CHO** se denomina **-carbaldehído**. Este tipo de nomenclatura es muy útil cuando el grupo aldehído va unido a un ciclo. La numeración del ciclo se realiza dando localizador 1 al carbono del ciclo que contiene el grupo aldehído.

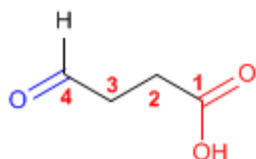


Ciclohexanocarbaldehído

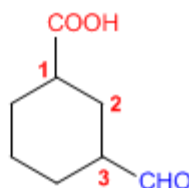


3-Bromociclopentanocarbaldehído

Regla 3. Cuando en la molécula existe un grupo prioritario al aldehído, este pasa a ser un sustituyente que se nombra como oxo- o formil-.



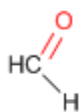
Ácido 4-oxobutanoico



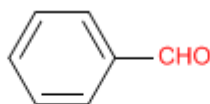
Ácido 3-formilciclohexanocarboxílico

Tanto **-carbaldehído** como **formil-** son nomenclaturas que incluyen el carbono del grupo carbonilo. **-carbaldehído** se emplea cuando el aldehído es grupo funcional, mientras que **formil-** se usa cuando actúa de sustituyente.

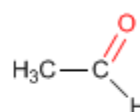
Regla 4. Algunos nombres comunes de aldehídos aceptados por la IUPAC son:



Formaldehído
(Metanal)

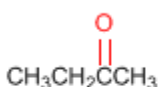


Benzaldehído
(Benceno**carbaldehído**)

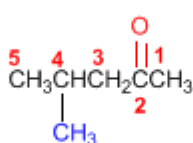


Acetaldehído
(Etanal)

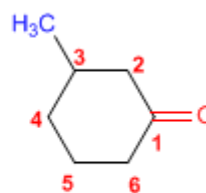
Regla 5. Las cetonas se nombran sustituyendo la terminación **-ano** del alcano con igual longitud de cadena por **-ona**. Se toma como cadena principal la de mayor longitud que contiene el grupo carbonilo y se numera para que éste tome el localizador más bajo.



Butan**ona**

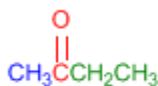


4-Metil-2-pentan**ona**

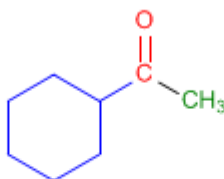


3-Metilciclohexan**ona**

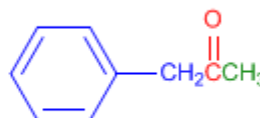
Regla 6. Existe un segundo tipo de nomenclatura para las cetonas, que consiste en nombrar las cadenas como sustituyentes, ordenándolas alfabéticamente y terminando el nombre con la palabra cetona.



Etil metil **cetona**

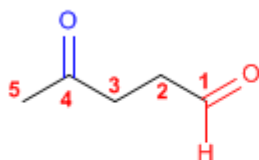


Ciclohexil metil **cetona**

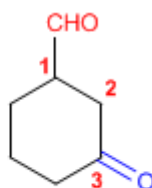


Fenil metil **cetona**

Regla 7. Cuando la cetona no es el grupo funcional de la molécula pasa a llamarse **OXO-**.



4-Oxopentan**al**

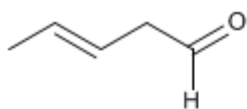


3-Oxociclohexano**carbaldehído**

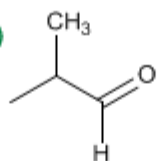
Nomenclatura de Aldehídos y Cetonas - Problema 9.1

Nombra los siguientes aldehídos y cetonas:

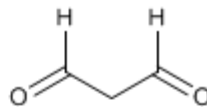
a)



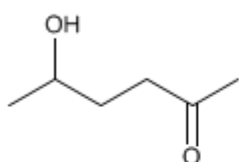
b)



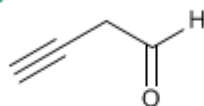
c)



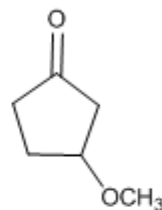
d)



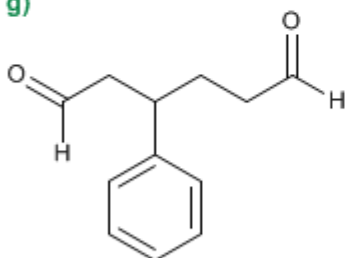
e)



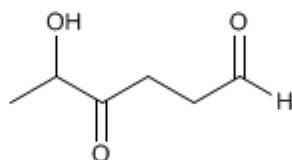
f)



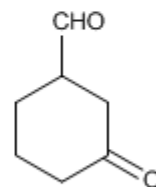
g)



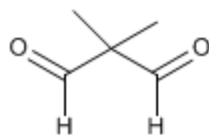
h)



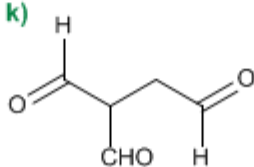
i)



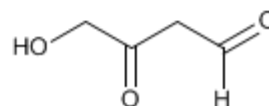
j)



k)

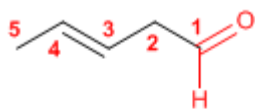


l)

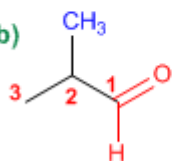


Solución

a)



b)



1. Cadena principal: 5 carbonos (pentano)

2. Numeración: comienza en el aldehído (grupo funcional)

Grupo funcional: aldehído

3. Nombre: Pent-3-enal

1. Cadena principal: 3 carbonos (propano)

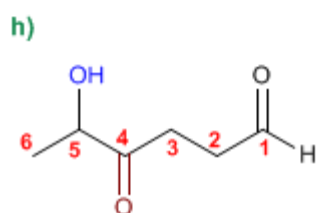
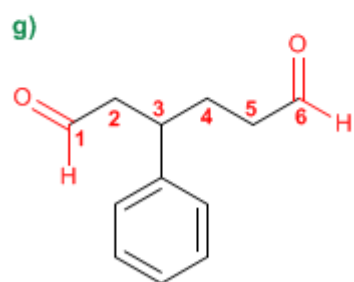
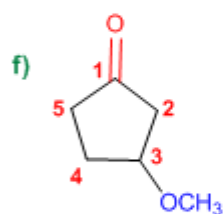
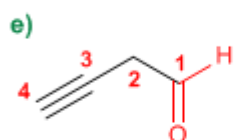
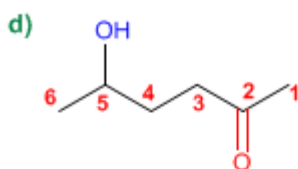
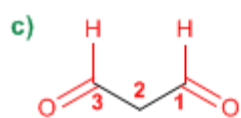
2. Numeración: localizador más bajo al aldehído.

3. Grupo funcional: aldehído

4. Sustituyentes: metilo en 2.

5. Nombre: 2-Metilpropanal

Los aldehídos y cetonas son prioritarios sobre alquenos y alquinos, y se numeran otorgándoles el localizador más bajo



1. Cadena principal: 3 carbonos (propano)
2. Grupo funcional: aldehído (dialdehído)
3. Nombre: Propanodial

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: cetona
3. Numeración: asignar el menor localizador a la cetona
4. Sustituyentes: hidroxí en 5.
5. Nombre: 5-Hidroxíhexan-2-ona

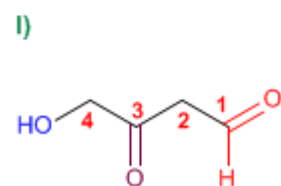
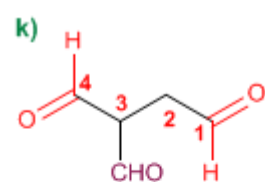
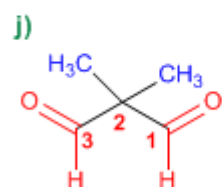
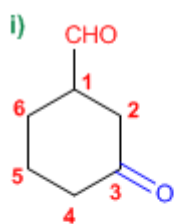
1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Nombre: But-3-inal

1. Cadena principal: ciclo de 5 miembros (ciclopentano)
2. Grupo funcional: cetona
3. Numeración: comienza en la cetona y prosigue hacia el sustituyente
4. Sustituyentes: metoxí en 3.
5. Nombre: 3-Metoxíciclopentanona

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: aldehído (dialdehído)
3. Numeración: comienza en el extremo que otorga al fenilo el localizador más bajo.
4. Sustituyentes: fenilo en 3.
5. Nombre: 3-Fenilhexanodial

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Sustituyentes: hidroxí en 5 y oxo en 4.
5. Nombre: 5-Hidroxí-4-oxohexanal

Los aldehídos son prioritarios sobre las cetonas que pasan a nombrarse como sustituyentes (oxo-)



1. Cadena principal: ciclo de 6 miembros (ciclohexano)
2. Grupo funcional: aldehído (-**carbaldehído**)
3. Numeración: menor localizador al grupo -**CHO** (este no se numera)
4. Sustituyentes: cetona (**oxo-**) en **3**
5. Nombre: **3-Oxociclohexanocarbaldehído**

1. Cadena principal: 3 carbonos (propano)
2. Grupo funcional: aldehído (dialdehído)
3. Sustituyentes: metilos en **2,2**.
4. Nombre: **2,2-Dimetilpropanodial**

1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Sustituyentes: formil en **3**
4. Nombre: **3-Formilbutanodial**

1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Sustituyentes: **hidroxi** en **4** y **oxo** en **3**.
5. Nombre: **4-Hidroxi-3-oxobutanal**

Nomenclatura de Aldehídos y Cetonas - Problema 9.2

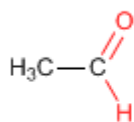
PRINT EMAIL

Dibuja la estructura de los siguientes aldehídos y cetonas:

- | | |
|---|----------------------------------|
| a) Etanal (acetaldehído) | g) 2,5-Dioxooctanodial |
| b) 3-Metilbutanal | h) 1,3-Ciclohexanodiona |
| c) Benzaldehído | i) 3-Metil-3-pental |
| d) 4-Hidroxyciclohexanocarbaldehído | j) 3-Oxobutanal |
| e) 3-Hidroxi-4-metil-5-oxociclohexanocarbaldehído | k) 3-Hidroxyciclopentanona |
| f) 2-Metil-2,5-octanodiona | l) 4-Etoxi-5-fenil-3-oxoheptanal |

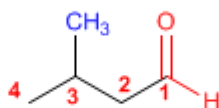
Solución

a)



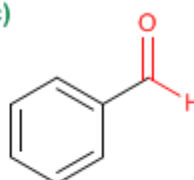
Etanal (acetaldehído)

b)

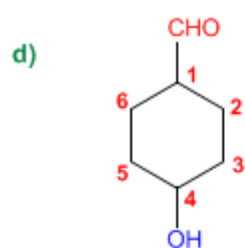


3-Metilbutanal

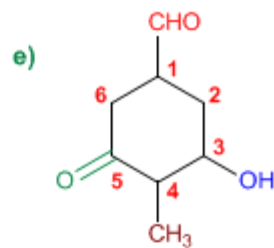
c)



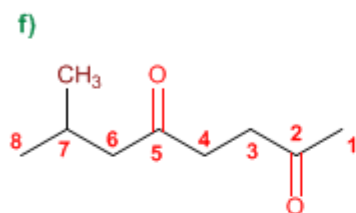
Benzaldehído



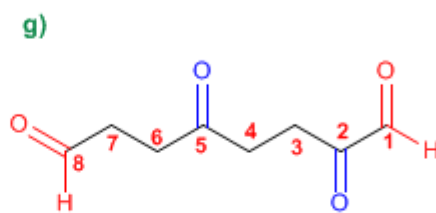
4-Hidroxiciclohexanocarbaldehído



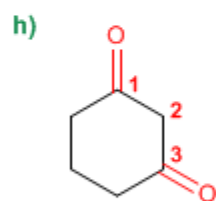
3-Hidroxi-4-metil-5-oxociclohexanocarbaldehído



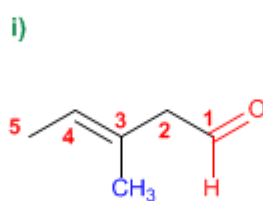
7-Metil-2,5-octanodiona



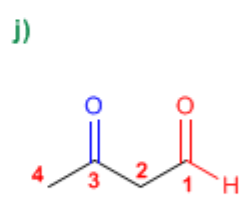
2,5-Dioxooctanal



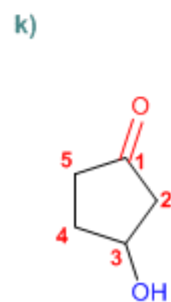
1,3-Ciclohexanodiona



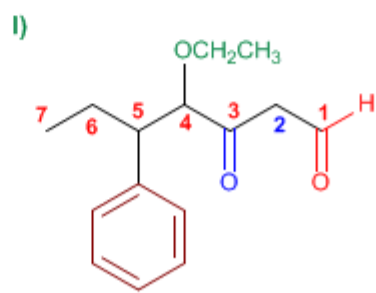
3-Metil-3-pentenal



3-Oxobutanal



3-Hidroxiciclopentanona

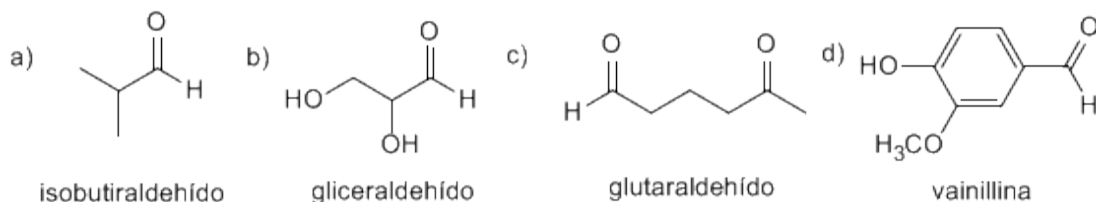


4-Etoxi-5-fenil-3-oxoheptanal

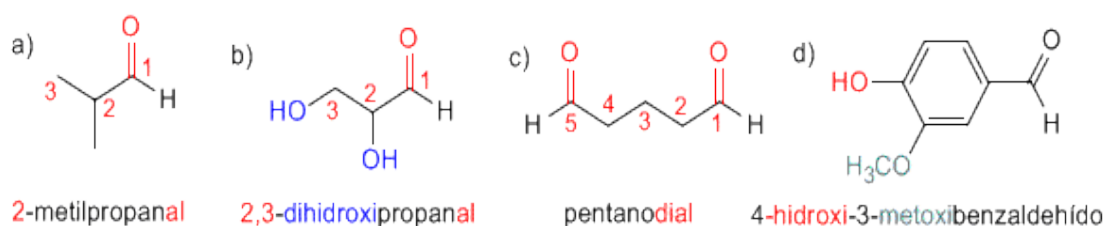
PROBLEMAS RESUELTOS DE ALDEHÍDOS Y CETONAS

Aldehídos y Cetonas: Problema 1

1) A continuación se dan nombres comunes y las fórmulas estructurales de algunos compuestos carbonílicos. Indique el nombre correspondiente según la IUPAC.



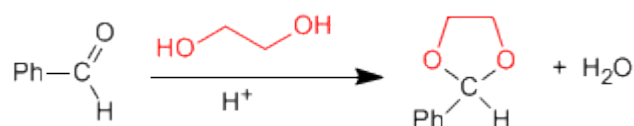
Solución



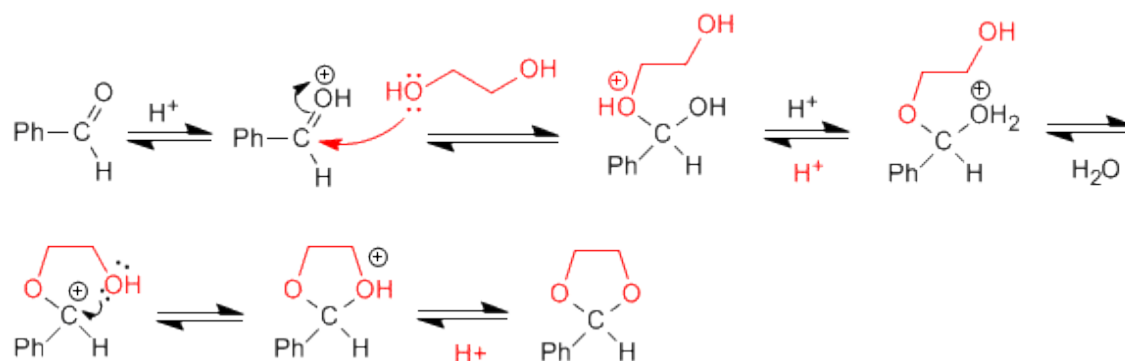
Aldehídos y cetonas: Problema 2

Dibuje la estructura del acetal que se forma cuando el benzaldehído se calienta con 1,2-etanodiol en medio ácido. Escriba un mecanismo detallado que justifique su formación. Describa paso a paso la hidrólisis de este acetal en medio ácido acuoso.

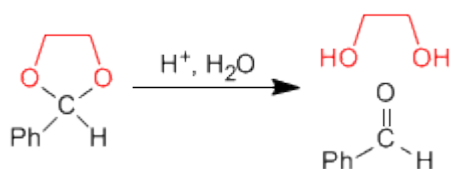
SOLUCIÓN



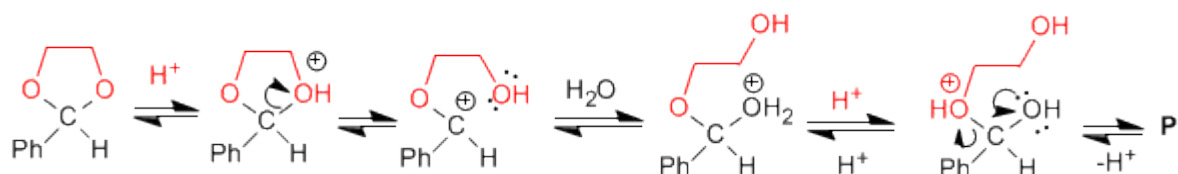
Mecanismo de formación del acetal:



La hidrólisis del acetal en medio ácido acuoso sigue es etapas inversas a la síntesis.



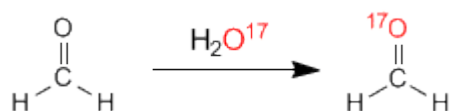
Mecanismo de hidrólisis del acetal cíclico.



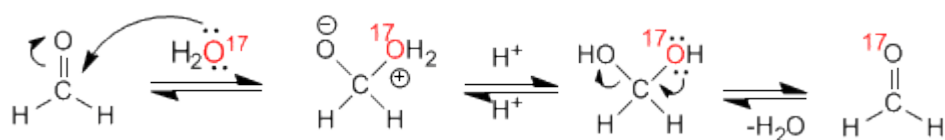
Aldehídos y Cetonas: Problema 3

Cuando se disuelve formaldehído en agua marcada con ^{17}O , se observa que después de unas horas tanto el hidrato del formaldehído como el formaldehído han incorporado el isótopo ^{17}O . Sugiera una explicación razonable de este hecho.

SOLUCION



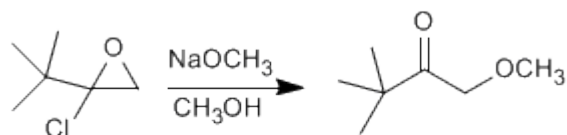
Mecanismo:



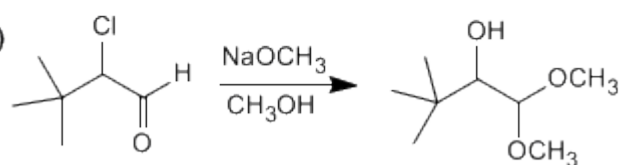
Aldehídos y Cetonas: Problema 4

Sugiera un mecanismo razonable para una de las siguientes reacciones:

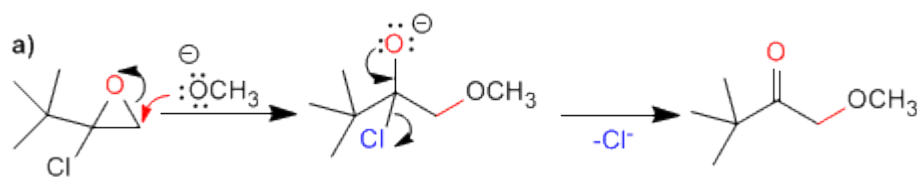
a)



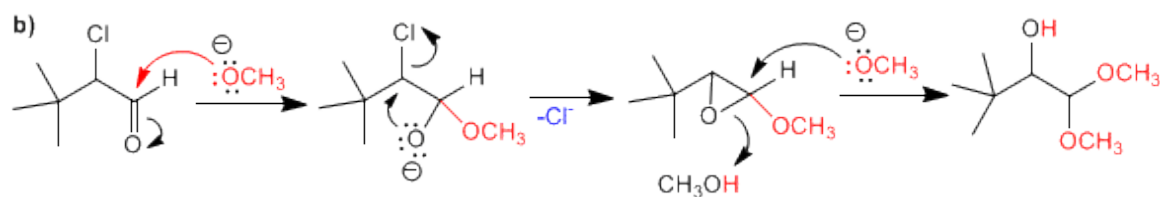
b)



SOLUCION



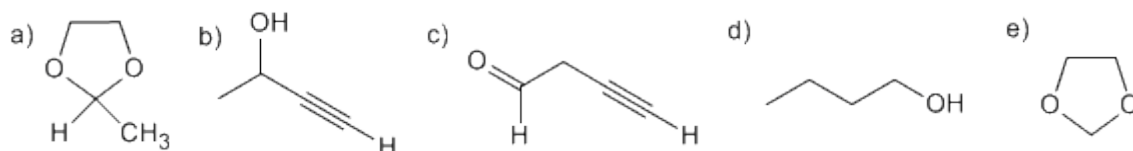
La primera etapa consiste en la apertura del oxaciclopropano sobre el carbono menos sustituido. En la segunda etapa, la cesión del par del oxígeno elimina el cloro, formándose un carbonilo.



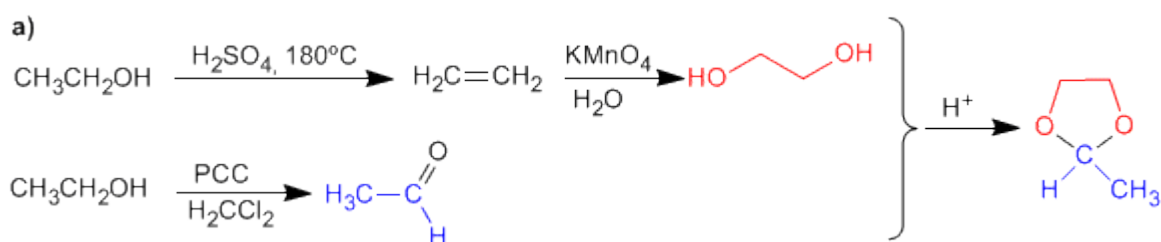
En el primer paso hay dos posibles posiciones de ataque; el carbono carbonilo y el carbono del cloro. Como el producto final no tiene metóxido en el carbono del cloro, atacamos al carbonilo. En la segunda etapa se produce una sustitución nucleófila intramolecular. Para terminar el metóxido abre el epóxido.

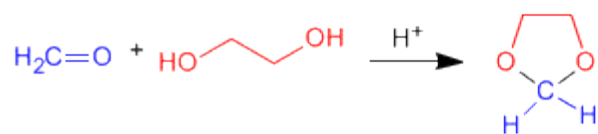
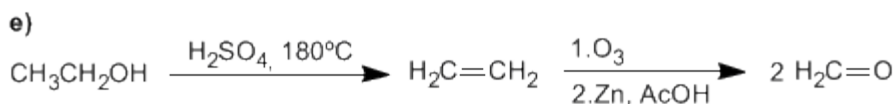
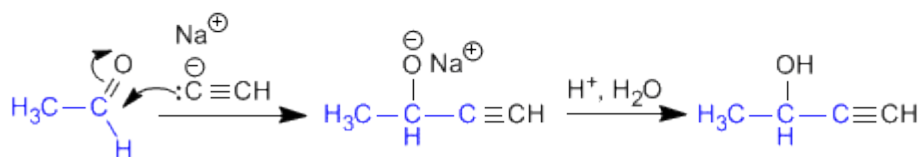
Aldehídos y Cetonas: Problema 5

Usando etanol como fuente de todos los átomos de carbono y los reactivos que necesite, describa una síntesis eficiente de cada una de las sustancias siguientes:

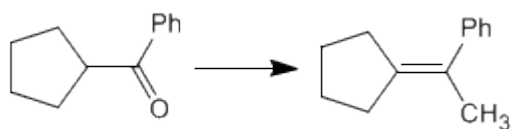


SOLUCIÓN

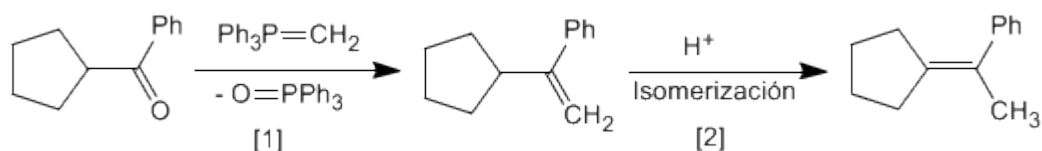




Utilizando los reactivos necesarios, indicar las etapas que permiten realizar la siguiente transformación:



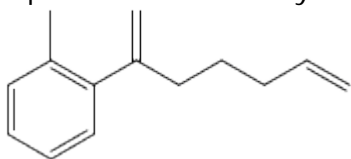
SOLUCIÓN



[2] Isomerización en medio ácido, impulsada por la mayor estabilidad del alqueno interno.

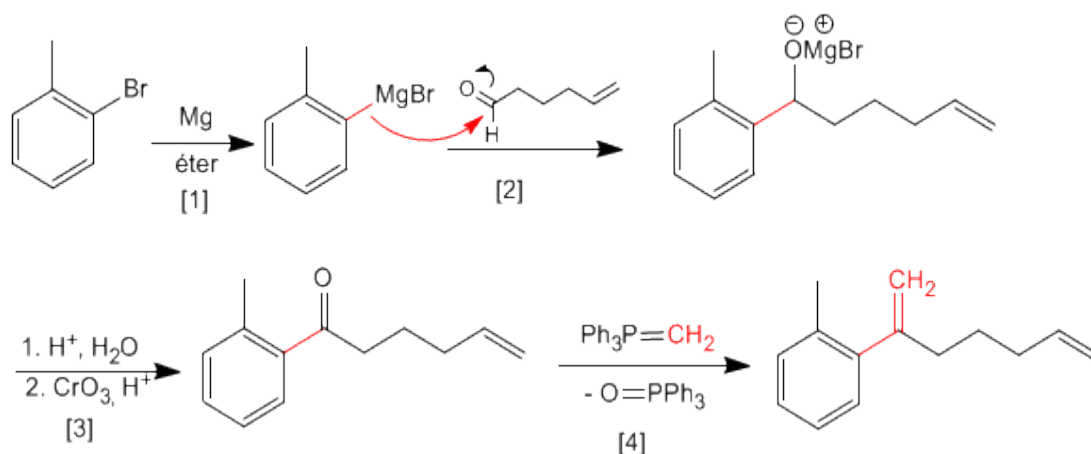
Aldehídos y Cetonas: Problema 7

A partir de 5-hexenal y o-bromotolueno obtener el siguiente producto.



Pueden ser necesarios reactivos orgánicos e inorgánicos adicionales.

SOLUCIÓN



[1] Formación del magnesiano

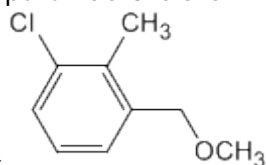
[2] Ataque nucleófilo del magnesiano al carbonilo.

[3] Hidrólisis y posterior oxidación del alcohol secundario.

[4] Reacción de Wittig entre la cetona y el trifenilmetilenfosforano.

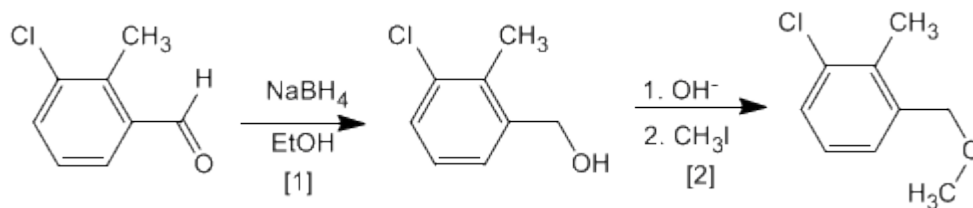
Aldehídos y Cetonas: Problema 8

Obtener a partir de 3-cloro-2-metilbenzaldehído y de los reactivos



necesarios
el compuesto siguiente:

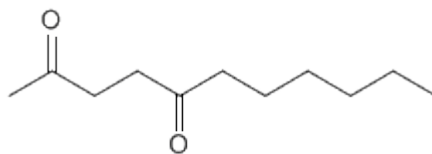
SOLUCIÓN



[1] Reducción del aldehído a alcohol

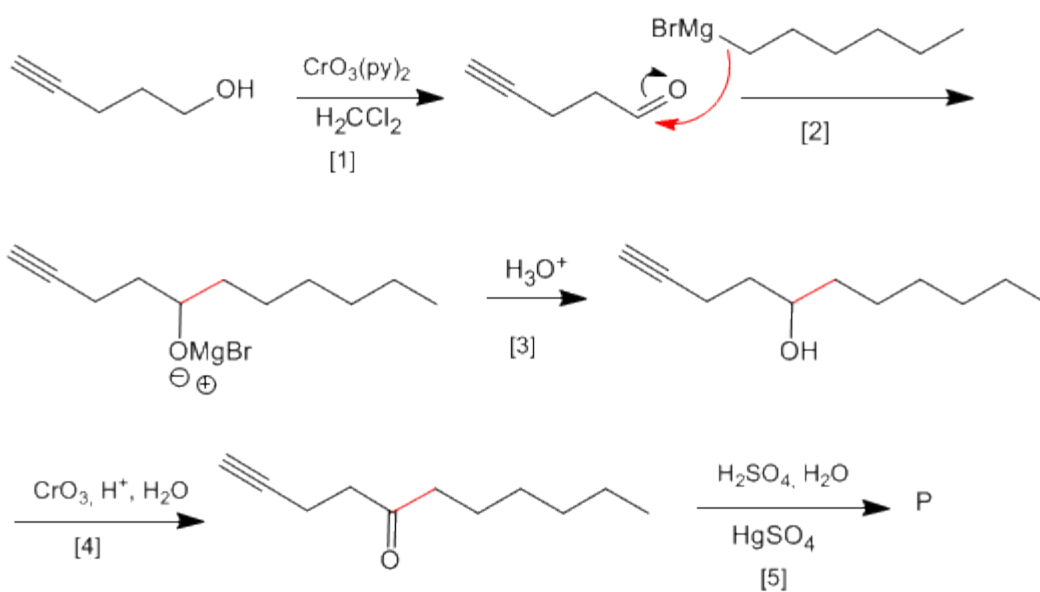
[2] Síntesis de Williamson de éteres.

Aldehídos y Cetonas: Problema 9



A partir de 4-pentin-1-ol obtener:

SOLUCIÓN

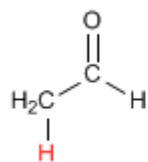


- [1] Oxidación del alcohol a aldehído
- [2] Formación del enlace carbono-carbono mediante organometálicos de magnesio
- [3] Protonación del alcohol
- [4] Oxidación del alcohol con Jones (Puedes utilizar también $\text{CrO}_3(\text{py})_2$)
- [5] Hidratación Markovnikov del alquino, para formar cetonas

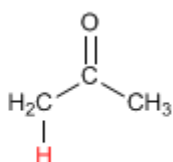
TEORÍA DE ENOLES Y ENOLATOS

Formación de Enolatos

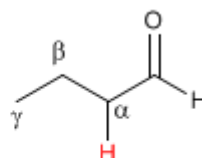
Los aldehídos y cetonas presentan hidrógenos ácidos en la posición vecina al grupo carbonilo, conocida como posición alfa. Estos hidrógenos presentan un pKa comprendido entre 18 y 21.



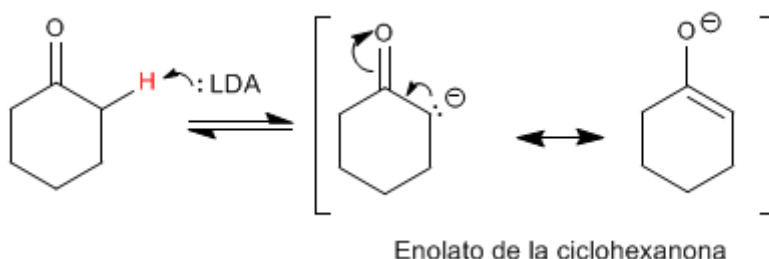
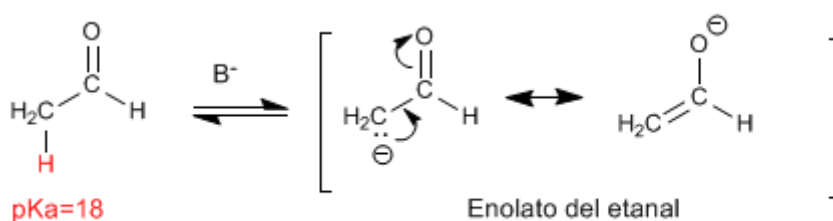
pKa=18



pKa=20-21



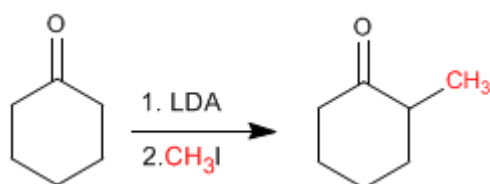
La acidez de los hidrógenos α es debida a la estabilización de la base conjugada (enolato) por resonancia.



Alquilación de Enolatos

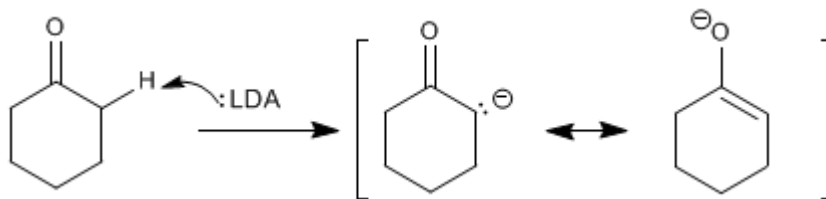
Los enolatos actúan como nucleófilos a través del carbono atacando a un gran número de electrófilos (haloalcanos, epóxidos, carbonilos, ésteres.....). En este punto nos fijaremos en la reacción entre enolatos y haloalcanos, que permite añadir cadenas carbonadas a la posición α de la cadena.

La Ciclohexanona se convierte en 2-Metilciclohexanona por tratamiento con LDA seguido de yoduro de metilo.

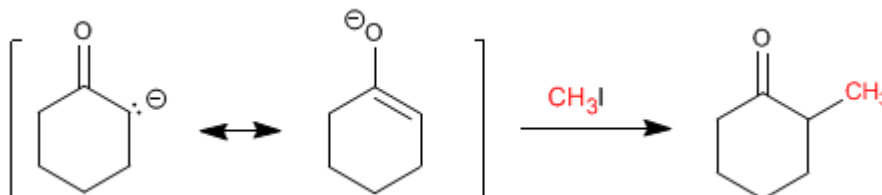


Etapas del mecanismo por el que se alquila la ciclohexanona:

Etapas 1. Formación del enolato

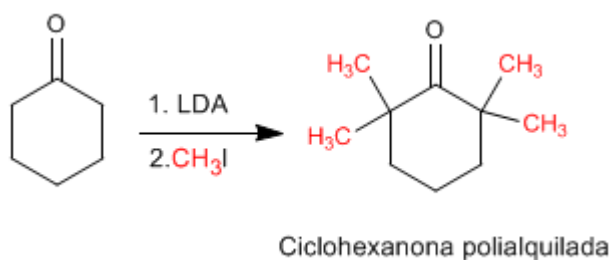


Etapas 2. Ataque nucleófilo del enolato sobre el haloalcano (Reacción de tipo S_N2)



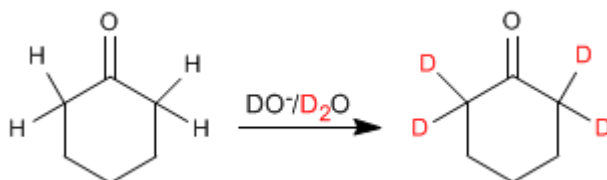
Las reacciones de alquilación tienen dos importantes problemas.

1. Competencia con la condensación aldólica. Los carbonilos en medio básico tienden a condensar para formar aldoles.
2. La reacción es difícil de controlar y tiende a polialquilar el carbonilo.



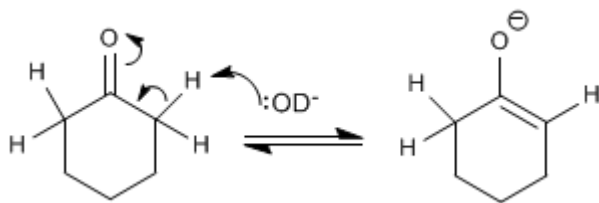
Intercambio hidrógeno - Deuterio

Los aldehídos y cetonas intercambian sus hidrógenos a por deuterios cuando se tratan con DO⁻/D₂O o con D⁺/D₂O. En medios básicos la reacción transcurre a través de enolatos y en medios ácidos los intermediarios formados son enoles.

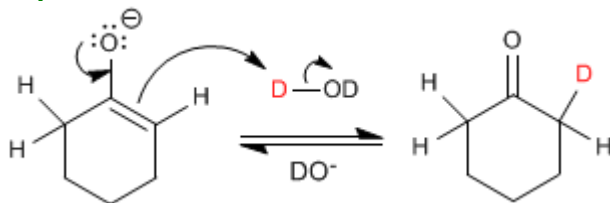


El mecanismo del intercambio hidrógeno-deuterio transcurre en los siguientes pasos:

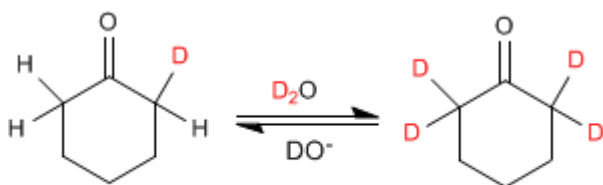
Etapas 1. Formación del enolato



Etapas 2. Transferencia del deuterio al enolato



Etapas 3. Sustitución del resto de hidrógenos



Halogenación de aldehídos y cetonas

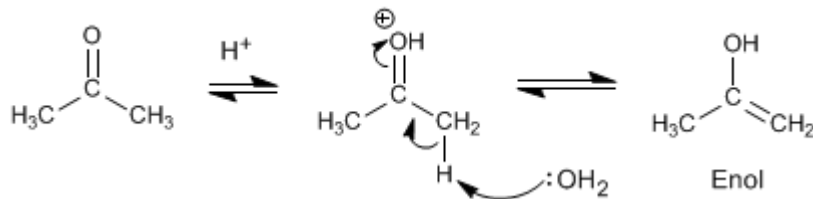
Los aldehídos y cetonas reaccionan con halógenos en medios ácidos o básicos produciéndose la sustitución de hidrógenos α por halógenos.

Halogenación de la propanona en medio ácido:

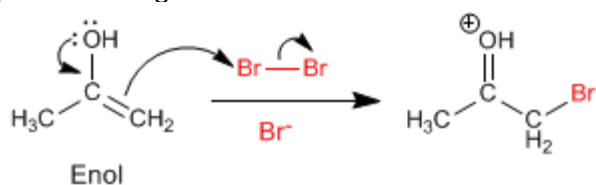


El mecanismo de halogenación en **medio ácido** tiene las siguientes etapas:

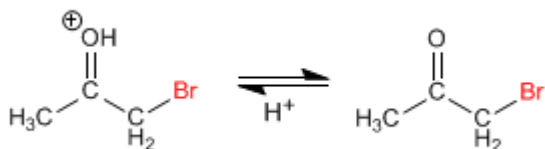
Etapas 1. Formación del enol



Etapas 2. Ataque nucleófilo del enol sobre el halógeno ayudado por la cesión del para del oxígeno.

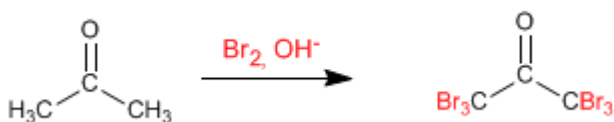


Etapa 3. Desprotonación



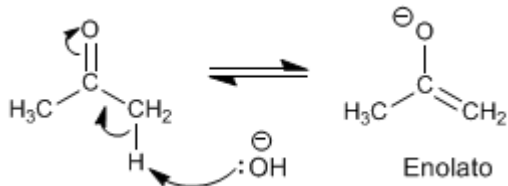
Trabajando con un equivalente de reactivo la halogenación para en una primera adición y no ocurren polihalogenaciones. El paso clave del mecanismo es la formación del enol y esta etapa requiere protonar el oxígeno del carbonilo. Una vez halogenada la posición α al oxígeno se vuelve menos básico, debido al efecto electronegativo del bromo, protonándose peor.

Halogenación de la propanona en **medio básico**:

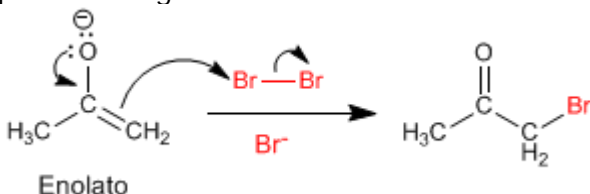


La halogenación en medio básico tiene el siguiente mecanismo:

Etapa 1. Formación del enolato



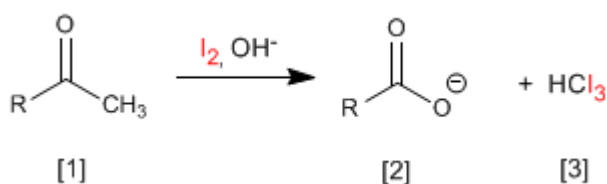
Etapa 2. Ataque nucleófilo del enolato sobre el halógeno ayudado por la cesión del par del oxígeno.



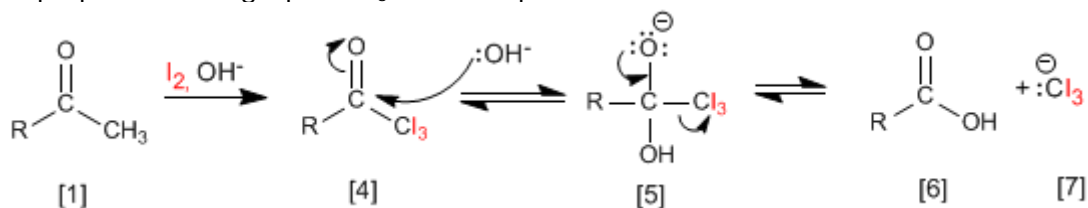
Este mecanismo se repite otras 5 veces sustituyendo todos los hidrógenos α por halógenos. En este caso la reacción no para puesto que el producto halogenado es más reactivo que la propanona de partida. La base arranca mejor los hidrógenos en el producto halogenado (son más ácidos), haciendo imposible parar la reacción.

Reacción del Haloformo (Yodoformo)

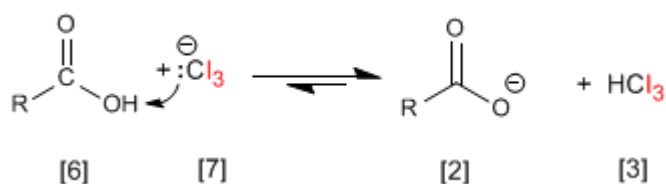
Las cetonas metílicas [1] reaccionan con halógenos en medios básicos generando carboxilatos [2] y haloformo [3].



El mecanismo consiste en halogenar completamente el metilo, sustituyendo en una etapa posterior el grupo -CX₃ formado por -OH.



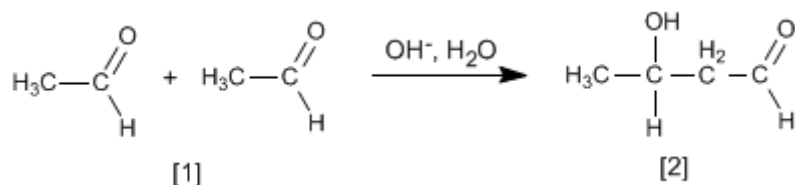
El grupo Cl₃⁻ es muy básico y desprotona el ácido carboxílico formándose yodoformo y el carboxilato.



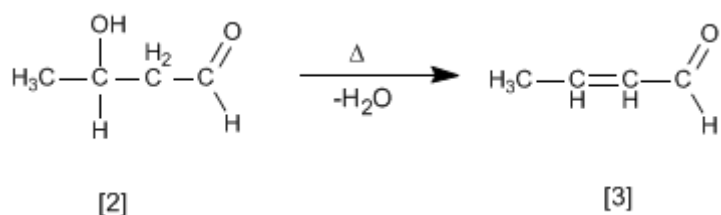
Esta reacción (con yodo) puede emplearse como ensayo analítico para identificar cetonas metílicas aprovechando que el yodoformo precipita de color amarillo.

Condensación Aldólica

Aldehídos y cetonas [1] condensan en medios básicos formando aldoles [2]. Esta reacción se denomina condensación aldólica.

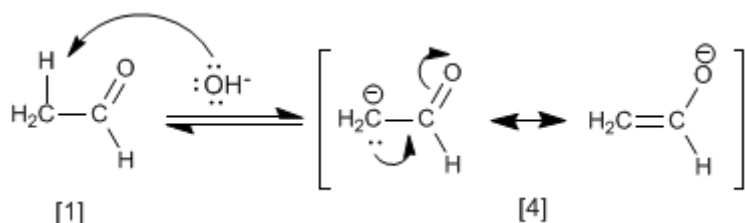


El aldol [2] formado deshidrata en el medio básico por calentamiento para formar un α,β-insaturado [3].



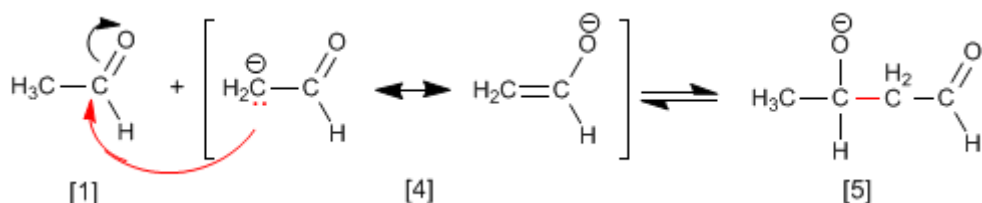
El mecanismo de la condensación aldólica transcurre con formación de un enolato, que ataca al carbonilo de otra molécula. En esta condensación se forma un enlace carbono-carbono entre el carbonilo de una molécula y el carbono α de la otra.

Etapas 1. Formación del enolato

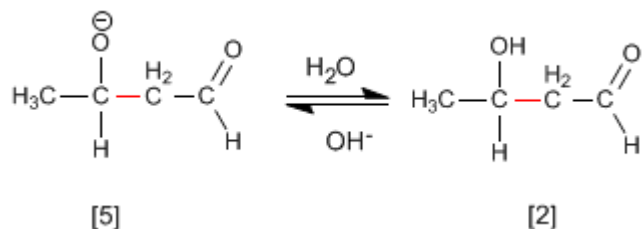


La base desprotona el carbono alfa del etanal [1] generando el enolato [4] estabilizado por resonancia.

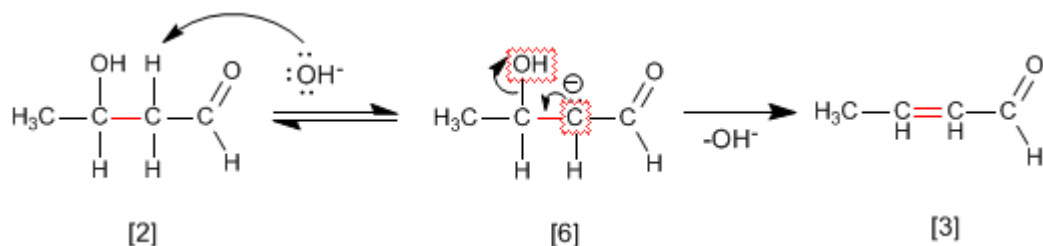
Etapas 2. Ataque nucleófilo del enolato sobre el carbonilo



Etapas 3. Protonación

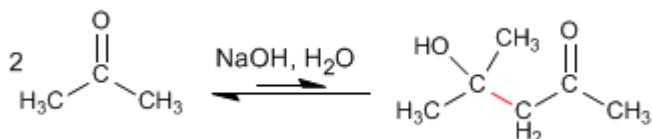


Etapas 4. Deshidratación del aldol

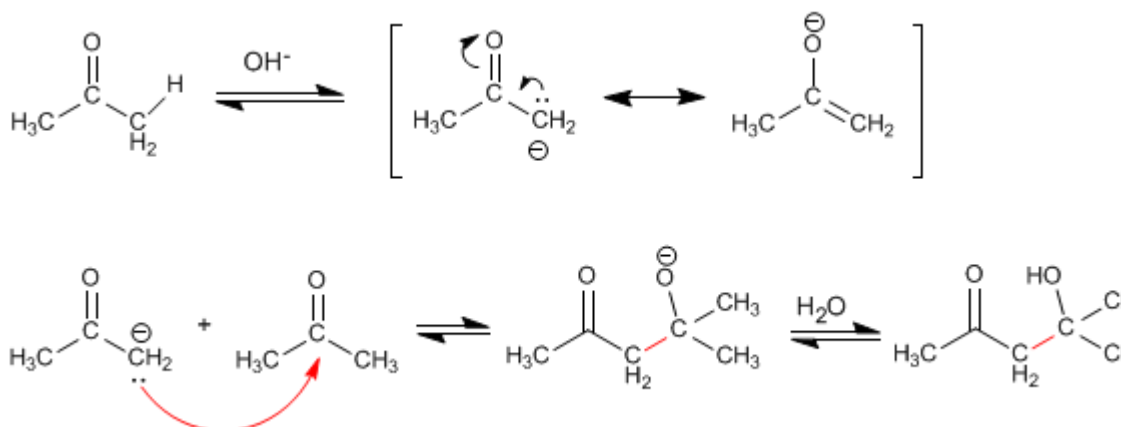


Condensación aldólica con cetonas

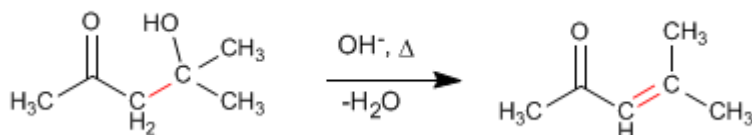
Las cetonas son menos reactivas que los aldehídos y dan un rendimiento muy bajo en la condensación aldólica. Así, dos moléculas de propanona condensan para formar el aldol correspondiente con un rendimiento del 2%. Se pueden conseguir porcentajes elevados del producto separándolo del medio de reacción según se va formando, o bien, calentando para deshidratarlo. De ambas formas los equilibrios de la aldólica se desplazan hacia el producto final.



Mecanismo de la reacción:

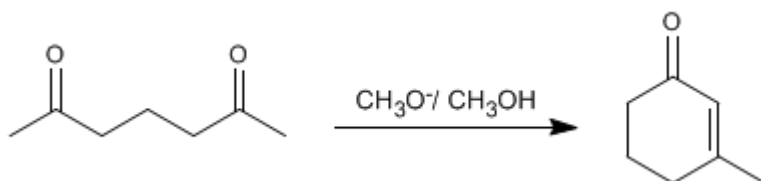


La deshidratación final permite el desplazamiento de los equilibrios. También se puede realizar una extracción del aldol del medio de reacción para favorecer la reacción.



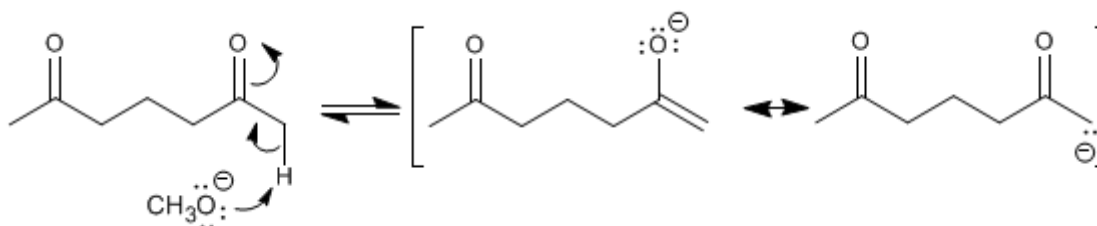
Condensación aldólica intramolecular

Los compuestos dicarbonílicos condensan mediante la aldólica intramolecular en medios básicos. En esta reacción se obtienen ciclos de cinco o seis miembros. Así, la 2,6-heptanodiona condensa con metóxido en metanol para formar el 3-metilciclohex-2-enona.

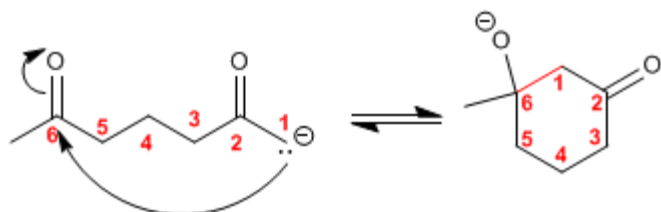


El mecanismo de la reacción transcurre a través de las siguientes etapas:

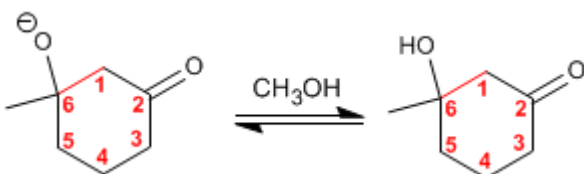
Etapa 1. Formación del enolato.



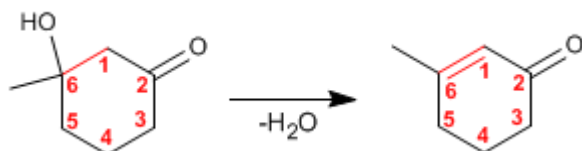
Etapa 2. Adición nucleófila intramolecular



Etapa 3. Protonación de la base del aldol



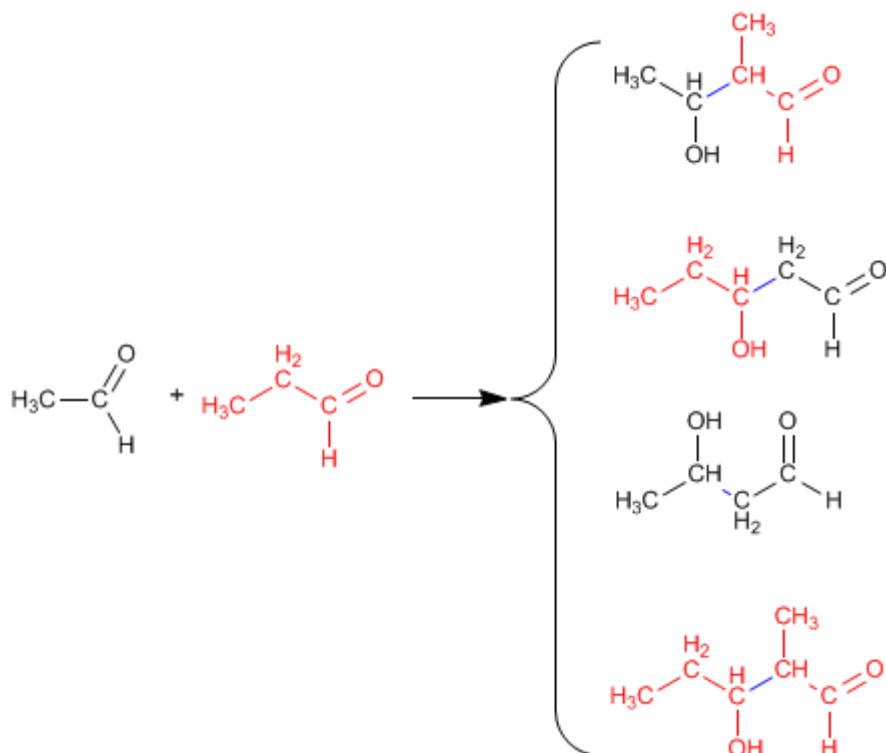
Etapa 4. Deshidratación del aldol



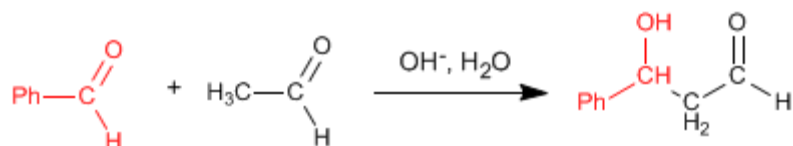
Condensación aldólica cruzada o mixta

La reacción entre dos carbonilos diferentes se llama aldólica cruzada o mixta. Esta reacción sólo tiene utilidad sintética en dos casos:

1. Sólo uno de los carbonilos puede formar enolatos.
 2. Uno de los carbonilos es mucho más reactivo que el otro.
- En el resto de situaciones la aldólica mixta genera mezclas de cuatro productos. Veamos como ejemplo la condensación del etanal y propanal.

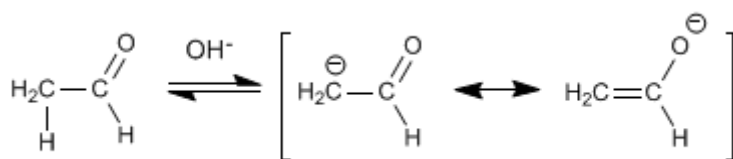


La condensación aldólica mixta del etanal con el benzaldehído genera un producto, cuando se trabaja en exceso de benzaldehído, debido a que el benzaldehído carece de hidrógenos en el carbono alfa y no puede formar enolatos.



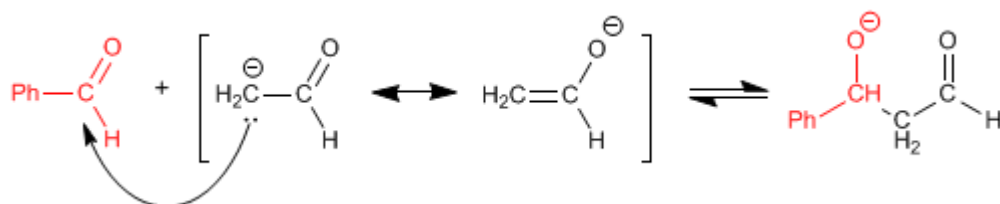
El mecanismo de esta reacción tiene lugar en las siguientes etapas:

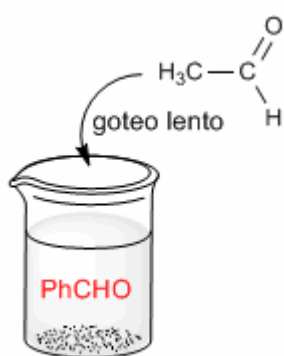
Etapla 1. Enolización del etanal



La formación de enolatos sólo puede tener lugar con el etanal, puesto que el benzaldehído carece de hidrógenos ácidos en el carbono alfa.

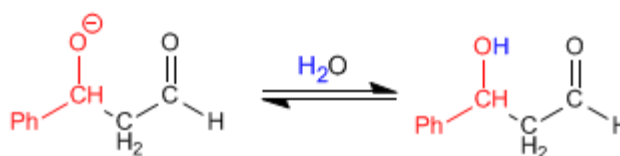
Etapla 2. Ataque nucleófilo del enolato al benzaldehído.





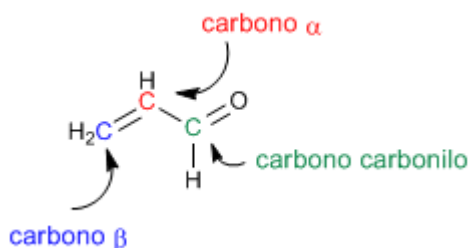
En esta etapa puede ocurrir el ataque del enolato de etanal sobre si mismo. Para evitarlo debe trabajarse en exceso de benzaldehído. Un procedimiento experimental muy usado para evitar la condensación del etanal consigo mismo es gotear lentamente el etanal sobre una disolución básica de benzaldehído

Etapa 3. Protonación



Síntesis de carbonilos alfa,beta-insaturados

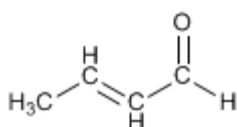
Los carbonilos α,β -insaturados son compuestos orgánicos que tienen un doble enlace entre las posiciones α,β de un aldehído o cetona.



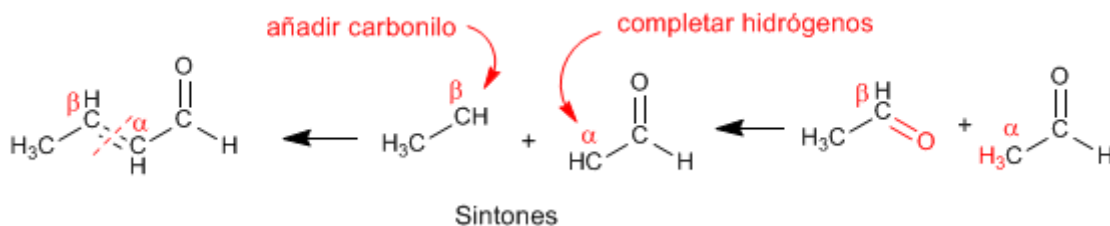
El propenal o acroleína es un carbonilo α,β -insaturado. Sus dos dobles enlaces conjugados le confieren una reactividad especial.

Existen 4 métodos importantes para la preparación de α,β -insaturados: condensación aldólica, halogenación del carbono α seguida de eliminación, oxidación de alcoholes alílicos y Wittig.

Método 1. Preparar mediante la condensación aldólica el siguiente compuesto.

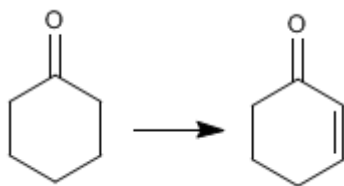


Empleamos la retrosíntesis para preparar el compuesto. Al ser de la familia de los α,β -insaturados se puede obtener mediante la condensación aldólica.

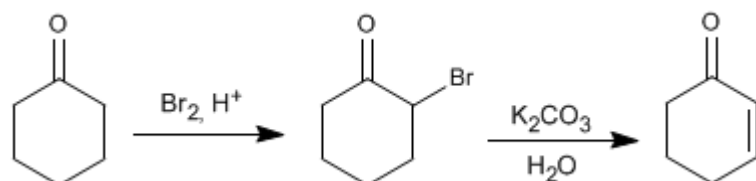


Para obtener los reactivos que forman el α,β -insaturado se rompe por el doble enlace, obteniéndose los sintones (equivalentes sintéticos). Los reactivos se obtienen añadiendo al carbono β un carbonilo y completando los hidrógeno que faltan en el carbono α .

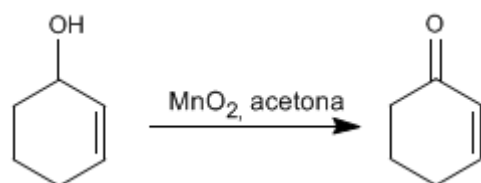
Ejemplo 2. Indicar como se puede realizar las siguiente transformación.



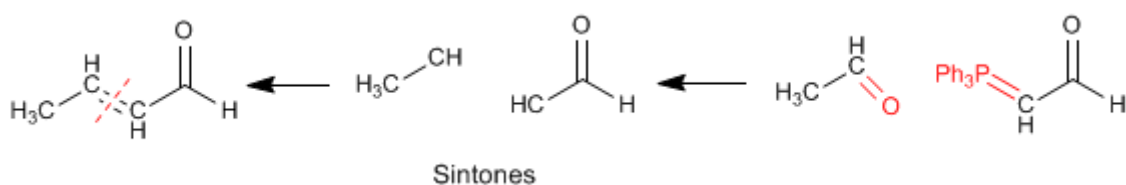
En una primera etapa se halogena la posición α del carbonilo. En la segunda etapa se realiza una eliminación que nos deja el producto final.



Método 3. La oxidación de alcoholes alílicos con dióxido de manganeso en acetona produce α,β -insaturados

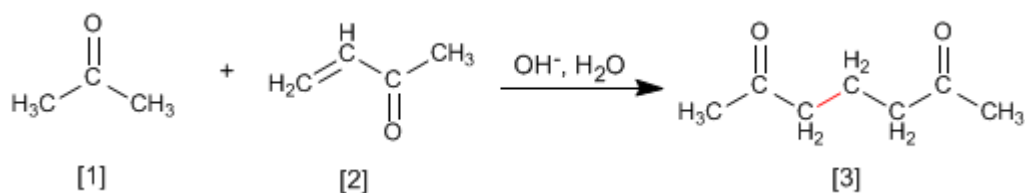


Método 4. Reacción de Wittig



Adición de Michael y anelación de Robinson

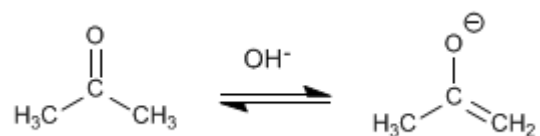
Los enolatos de aldehídos o cetonas se adicionan a los α,β -insaturados para formar 1,5-dicarbonilos. Esta reacción se denomina adición de Michael.



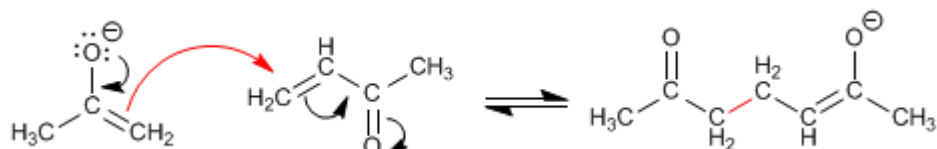
La propanona [1] reacciona con el α,β -insaturado [2] para formar el 1,5-dicarbonilo [3]

Mecanismo de la Adición de Michael:

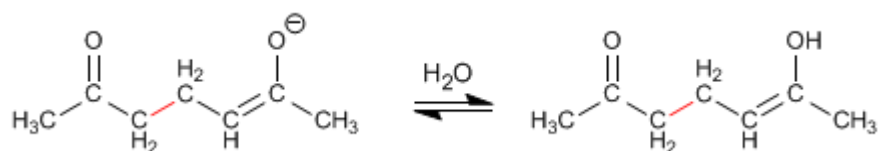
Etapla 1. Formación del enolato.



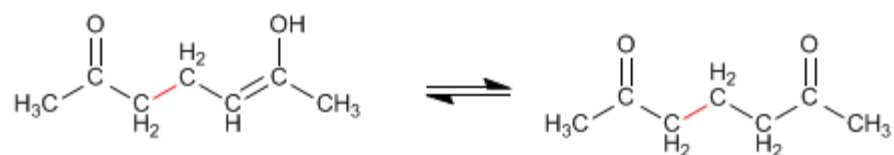
Etapla 2. Ataque nucleófilo del enolato al carbono β del α,β -insaturado.



Etapla 3. Equilibrio ácido-base



Etapla 4. Tautomería ceto-enol



El producto de Michael puede condensar mediante una aldólica intramolecular, formando un α,β -insaturado. El conjunto de la adición de Michael y la aldólica final se conoce como reacción de Robinson

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Química Orgánica

Recopilación : 2da Edición - 2009

José A.

Química Orgánica

Recopilación: 2da Edición

Diciembre 2009

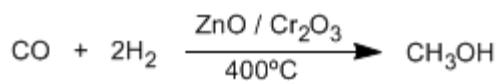
Índice:

- i. Alcoholes*
- ii. Éteres*
- iii. Aldehídos y Cetonas*
- iv. Enoles y Enolatos*
- v. Benceno*

SÍNTESIS Y REACTIVIDAD DE ALCOHOLES

Alcoholes - características generales

Los alcoholes son compuesto orgánicos que contienen el grupo hidroxilo (-OH). El metanol es el alcohol más sencillo, se obtiene por reducción del monóxido de carbono con hidrógeno.

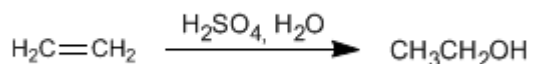


El metanol es un líquido incoloro, su punto de ebullición es 65°C, miscible en agua en todas las proporciones y venenoso (35 ml pueden matar una persona)

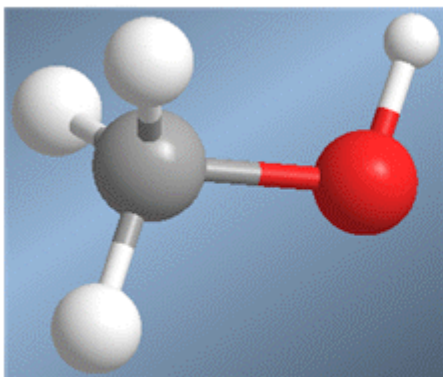
La mitad del metanol producido se oxida a metanal (formaldehído), material de partida para la fabricación de resinas y plásticos.

El etanol se obtiene por fermentación de materia vegetal, obteniéndose una concentración máxima de 15% en etanol. Por destilación se puede aumentar esta concentración hasta el 98%.

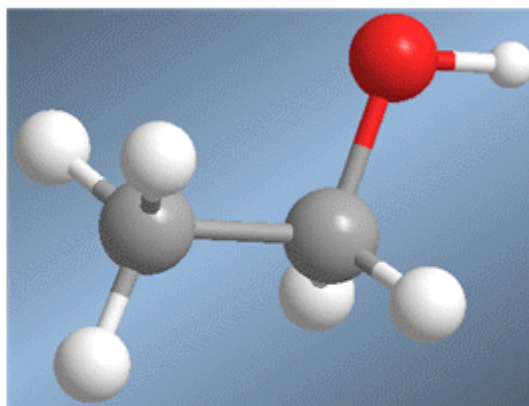
También se puede obtener etanol por hidratación del etileno (eteno) que se obtiene a partir del petróleo.



El etanol es un líquido incoloro, miscible en agua en todas proporciones, con punto de ebullición de 78°C. Es fácilmente metabolizado por nuestros organismos, aunque su abuso causa alcoholismo.



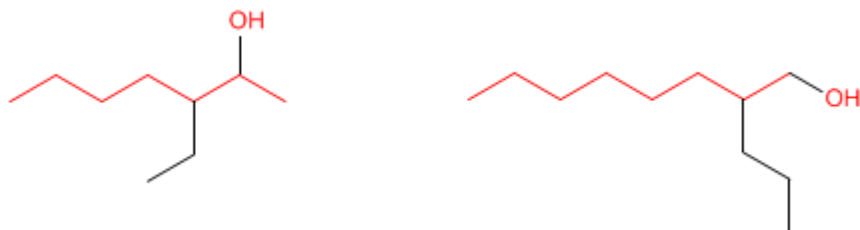
(metanol) CH_3OH



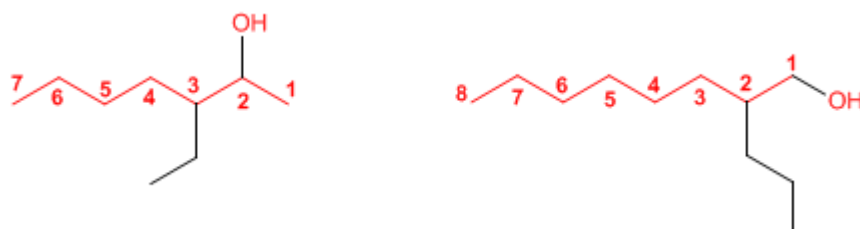
(etanol) $\text{CH}_3\text{CH}_2\text{OH}$

Nomenclatura de Alcoholes

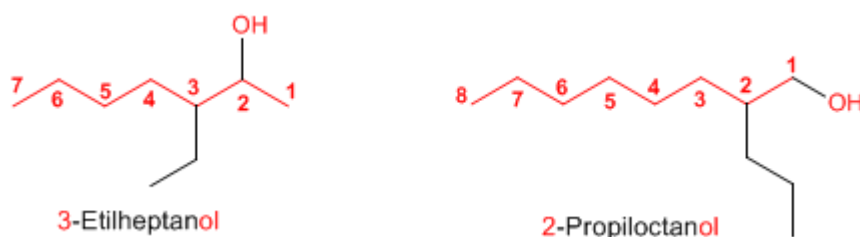
Regla 1. Se elige como cadena principal la de mayor longitud que contenga el grupo -OH.



Regla 2. Se numera la cadena principal para que el grupo -OH tome el localizador más bajo. El grupo hidroxilo tiene preferencia sobre cadenas carbonadas, halógenos, dobles y triples enlaces.



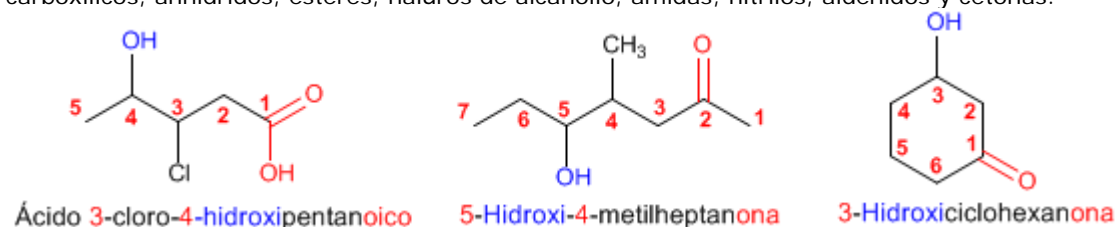
Regla 3. El nombre del alcohol se construye cambiando la terminación -o del alcano con igual número de carbonos por -ol



3-Etilheptanol

2-Propiloctanol

Regla 4. Cuando en la molécula hay grupos funcionales de mayor prioridad, el alcohol pasa a ser un mero sustituyente y se llama **hidroxi-**. Son prioritarios frente a los alcoholes: ácidos carboxílicos, anhídridos, ésteres, haluros de alcanoilo, amidas, nitrilos, aldehídos y cetonas.

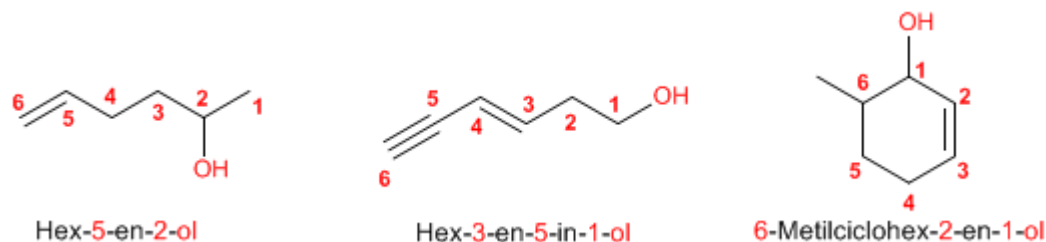


Ácido 3-cloro-4-hidroxi-pentanoico

5-Hidroxi-4-metilheptanona

3-Hidroxiciclohexanona

Regla 5. El grupo -OH es prioritario frente a los alquenos y alquinos. La numeración otorga el localizador más bajo al -OH y el nombre de la molécula termina en -ol.



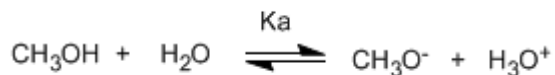
Hex-5-en-2-ol

Hex-3-en-5-in-1-ol

6-Metilciclohex-2-en-1-ol

Acidez y basicidad de alcoholes

Los alcoholes son especies anfóteras (anfipróticas), pueden actuar como ácidos o bases. En disolución acuosa se establece un equilibrio entre el alcohol, el agua y sus bases conjugadas.



Escribiendo la constante del equilibrio (K_a)

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{O}^-]}{[\text{CH}_3\text{OH}]} = 10^{-15.5}$$

El pequeño valor de la constante nos indica que el equilibrio está totalmente desplazado a la izquierda.

El logaritmo cambiado de signo de la constante de equilibrio nos da el pK_a del metanol, parámetro que indica el grado de acidez de un compuesto orgánico.

$$pK_a = -\log k_a = 15.5$$

El aumento del pK_a supone una disminución de la acidez. Así, el metanol con un pK_a de 15.5 es ligeramente más ácido que el etanol con pK_a de 15.9.

El pK_a de los alcoholes se ve influenciado por algunos factores como son el tamaño de la cadena carbonada y los grupos electronegativos

Al aumentar el tamaño de la cadena carbonada el alcohol se vuelve menos ácido.

CH_3OH	$pK_a = 15.5$	
$\text{CH}_3\text{CH}_2\text{OH}$	$pK_a = 15.9$	
$(\text{CH}_3)_2\text{CHOH}$	$pK_a = 17.1$	
$(\text{CH}_3)_3\text{COH}$	$pK_a = 18$	

Los grupos electronegativos (halógenos) aumentan la acidez de los alcoholes (bajan el pK_a)

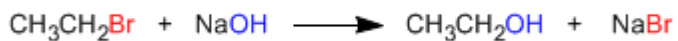
$\text{CH}_3\text{CH}_2\text{OH}$	$pK_a = 15.9$	
$\text{ClCH}_2\text{CH}_2\text{OH}$	$pK_a = 14.3$	
$\text{F}_3\text{CCH}_2\text{OH}$	$pK_a = 12.4$	

Síntesis de Alcoholes a partir de Haloalcanos

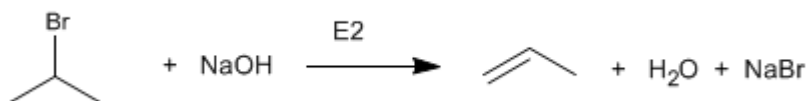
Los alcoholes se pueden obtener a partir de haloalcanos mediante reacciones S_N2 y S_N1

Síntesis de alcoholes mediante S_N2

Los haloalcanos primarios reaccionan con hidróxido de sodio para formar alcoholes. Haloalcanos secundarios y terciarios eliminan para formar alquenos.

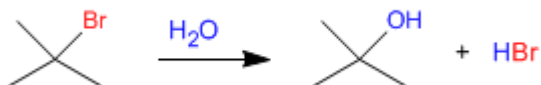


El bromuro de isopropilo (sustrato secundario) elimina al reaccionar con el ión hidróxido.



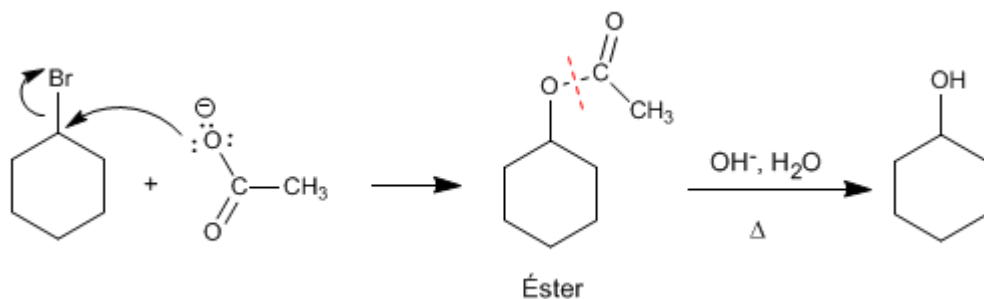
Síntesis de alcoholes mediante S_N1

Los sustratos secundarios y terciarios reaccionan con agua mediante mecanismo S_N1 para formar alcoholes.



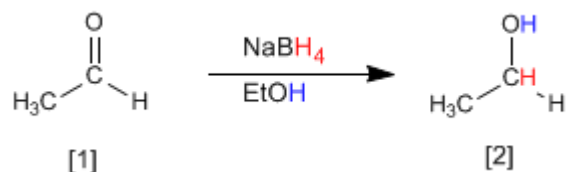
Hidrólisis de ésteres

Es un método interesante para preparar alcoholes a partir de haloalcanos secundarios. El haloalcano se convierte en éster por reacción con acetato de sodio, para después hidrolizarse en medio ácido o básico, obteniéndose el alcohol.



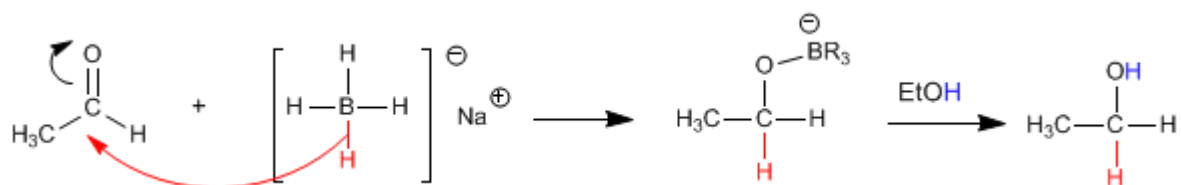
Síntesis de Alcoholes por reducción de carbonilos

Tanto el borohidruro de sodio (NaBH_4) como el hidruro de litio y aluminio (LiAlH_4) reducen aldehídos y cetonas a alcoholes.

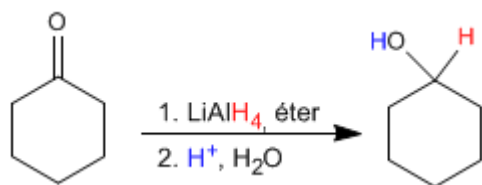


El etanal [1] se transforma por reducción con el borohidruro de sodio en etanol [2].

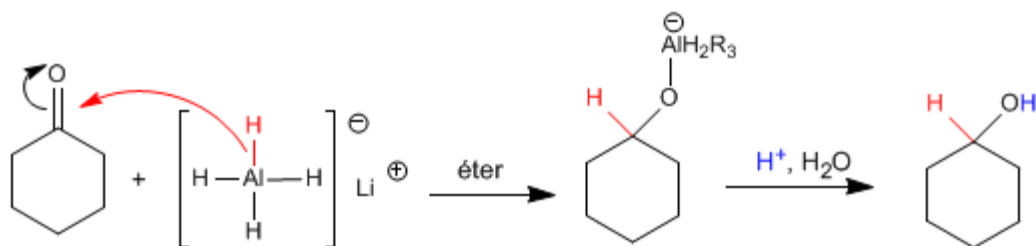
El mecanismo transcurre por ataque del hidruro procedente del reductor sobre el carbono carbonilo. En una segunda etapa el disolvente protona el oxígeno del alcóxido.



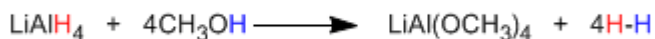
El hidruro de litio y aluminio trabaja en medio éter y transforma aldehídos y cetonas en alcoholes después de una etapa de hidrólisis ácida.



El mecanismo es análogo al del borohidruro de sodio.



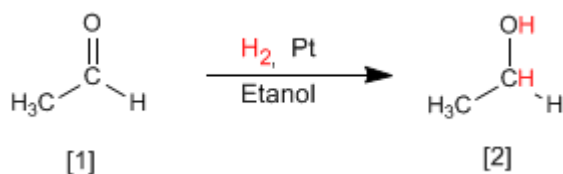
El reductor de litio y aluminio es más reactivo que el de boro, reacciona con el agua y los alcoholes desprendiendo hidrógeno. Por ello, debe disolverse en medios apróticos (éter).



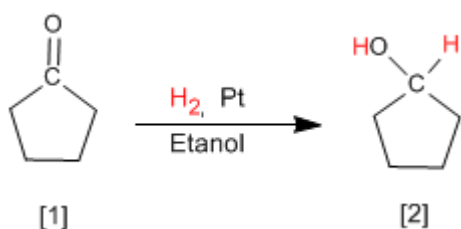
El reductor de boro, menos reactivo, descompone lentamente en medios próticos, lo que permite utilizarlo disuelto en etanol o agua.

Síntesis de Alcoholes por hidrogenación de Carbonilos

Otro método para preparar alcoholes consiste en la reducción de aldehídos o cetonas a alcoholes. El método más simple es la hidrogenación del doble enlace carbono-oxígeno, utilizando hidrógeno en presencia de un catalizador de platino, paladio, níquel o rutenio.



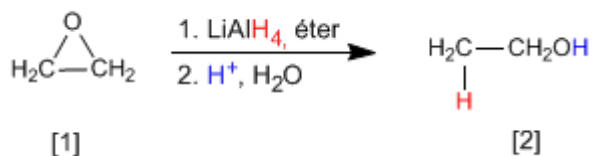
El etanal [1] se transforma por hidrogenación del doble enlace en etanol [2]



La ciclopentanona [1] se transforma por hidrogenación en ciclopentanol [2]

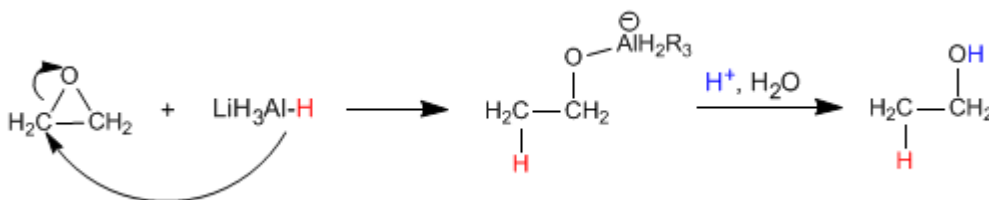
Síntesis de Alcoholes a partir de Epóxidos

Los alcoholes se pueden obtener por apertura de epóxidos (oxaciclopropanos). Esta apertura se puede realizar empleando reactivos organometálicos o el reductor de litio y aluminio.



El oxaciclopropano [1] se transforma por reducción con hidruro de litio y aluminio en etanol [2].

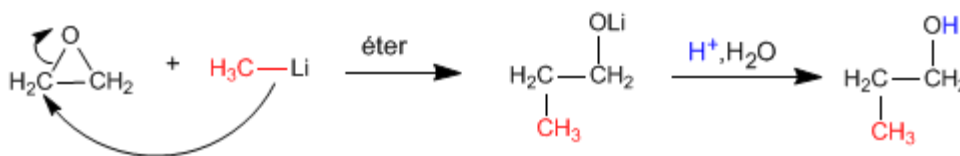
El mecanismo de la reacción comienza con el ataque del hidruro procedente del reductor sobre el carbono polarizado positivamente del epóxido, para terminar con la protonación del alcóxido.



Los reactivos de Grignard (organometálicos de magnesio) y los organolíticos reaccionan con oxaciclopropano para dar un alcohol primario.



El metililitio ataca al oxaciclopropano [1] para formar propan-1-ol [2].

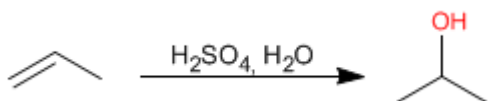


Síntesis de Alcoholes por Hidratación de Alquenos

Un método de síntesis para alcoholes, ya estudiado en la sección de alquenos, consiste en hidratar el alqueno. La adición del -OH puede ser en el carbono más sustituido del alqueno (Markovnikov), o bien, en el carbono menos sustituido (antiMarkovnikov).

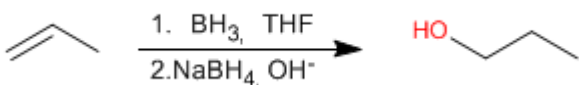
Hidratación Markovnikov

En esta hidratación el grupo hidroxilo va al carbono con más sustituyentes. Se emplea como reactivo sulfúrico acuoso, o bien, acetato de mercurio en agua, seguido de reducción con borohidruro de sodio.



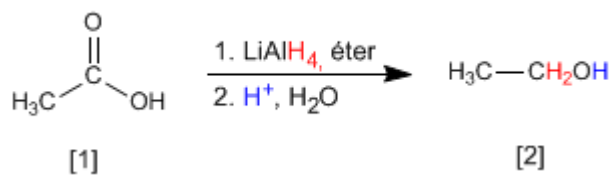
Hidratación antiMarkovnikov

El grupo hidroxilo se adiciona al carbono menos sustituido. El reactivo empleado es borano en THF seguido de oxidación con agua oxigenada en medio básico (hidroboración)

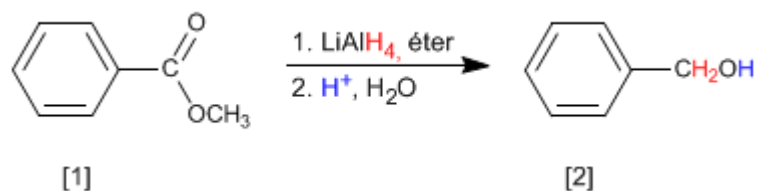


Síntesis de alcoholes por reducción de ácidos y ésteres

Los ácidos carboxílicos y los ésteres se reducen a alcoholes con el hidruro de litio y aluminio.
Reductores más suaves como el borohidruro de sodio son incapaces de reducir estos compuestos.



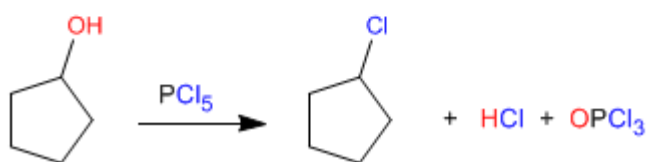
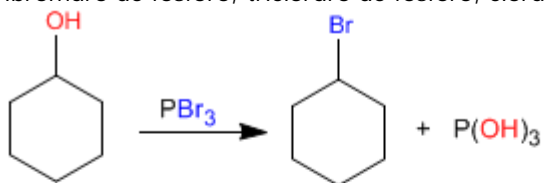
El ácido etanoico [1] se transforma por reducción con hidruro de litio y aluminio en etanol [2].



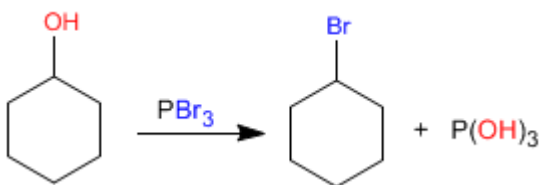
El benzoato de metilo [1] se transforma en alcohol bencílico [2] por reducción con hidruro de litio y aluminio.

Síntesis de Haloalcanos a partir de Alcoholes

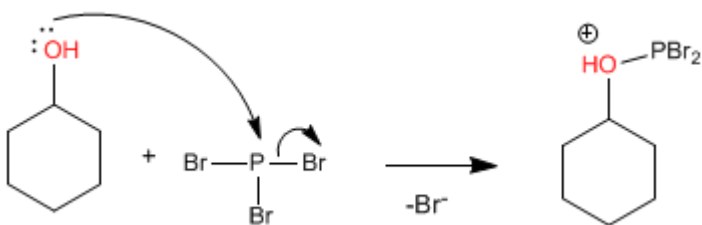
Los alcoholes primarios y secundarios pueden convertirse en haloalcanos con reactivos como: tribromuro de fósforo, tricloruro de fósforo, cloruro de tionilo y pentacloruro de fósforo.



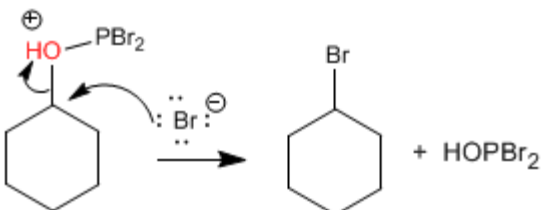
El mecanismo de estas reacciones es de tipo $\text{S}_{\text{N}}2$ y sólo los alcoholes primarios y secundarios reaccionan. Veamos el mecanismo de la primera reacción.



Etapas 1. Ataque del alcohol al tribromuro de fósforo



Etapas 2. Sustitución nucleófila bimolecular, actuando el bromuro como nucleófilo

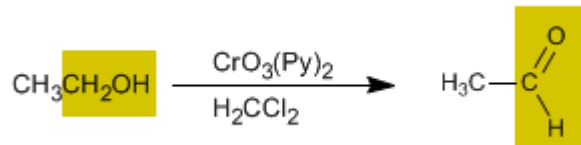


Todos los bromos del PBr_3 son reactivos y el mecanismo se repite dos veces más.

Oxidación de Alcoholes

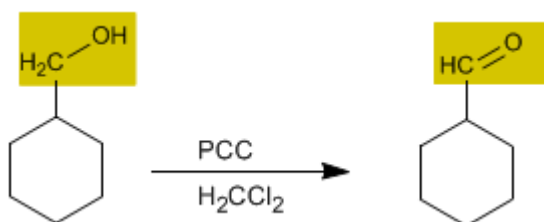
La oxidación de alcoholes forma compuestos carbonilos. Al oxidar alcoholes primarios se obtienen aldehídos, mientras que la oxidación de alcoholes secundarios forma cetonas.

Oxidación de alcoholes primarios a aldehídos



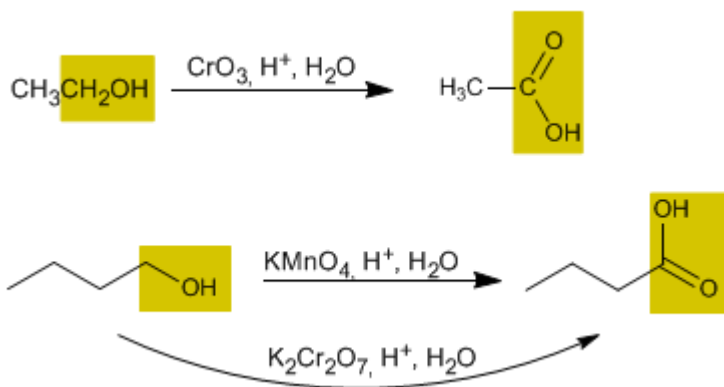
El trióxido de cromo con piridina en diclorometano permite aislar aldehídos con buen rendimiento a partir de alcoholes primarios.

Se conoce como PCC (clorocromato de piridinio) al trióxido de cromo con piridina y ácido clorhídrico en diclorometano. Este reactivo también convierte alcoholes primarios en aldehídos.



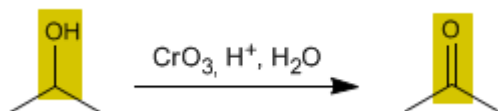
Oxidación de alcoholes primarios a ácidos carboxílicos

El trióxido de cromo en medio ácido acuoso (reactivo de Jones), el permanganato de potasio y el dicromato de potasio oxidan los alcoholes primarios a ácidos carboxílicos.



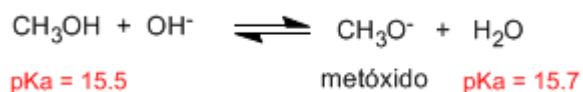
Oxidación de alcoholes secundarios a cetonas

Los oxidantes convierten los alcoholes secundarios en cetonas. No es posible la sobreoxidación a ácido carboxílico.

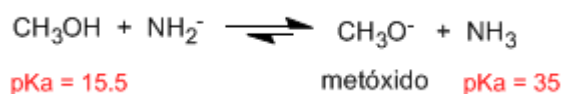


Formación de Alcóxidos a partir de Alcoholes

Los alcóxidos son las bases de los alcoholes, se obtienen por reacción del alcohol con una base fuerte.

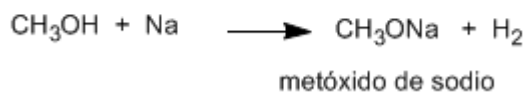
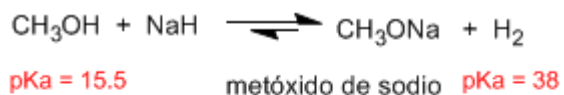


Los pKa de los ácidos conjugados son similares y el equilibrio no se encuentra desplazado. El ión hidróxido es una base demasiado débil para formar el alcóxido en cantidad importante.



El amiduro es una base muy fuerte y desplaza el equilibrio a la derecha, transformando el metanol en metóxido.

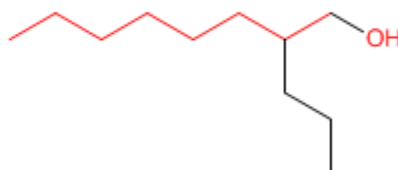
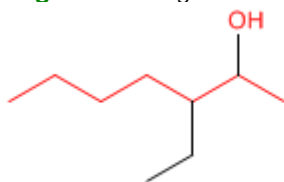
Otras bases fuertes que pueden ser usadas para formar alcóxidos son: hidruro de sodio, LDA, sodio metal.



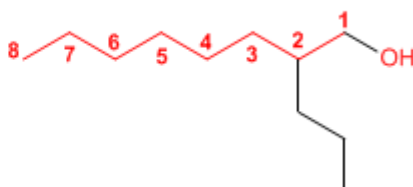
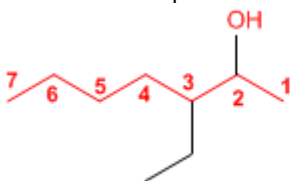
PROBLEMAS NOMENCLATURA - ALCOHOLES

Nomenclatura de Alcoholes - Reglas IUPAC

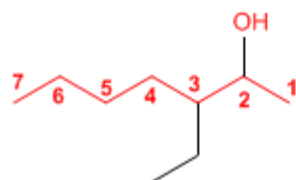
Regla 1. Se elige como cadena principal la de mayor longitud que contenga el grupo -OH.



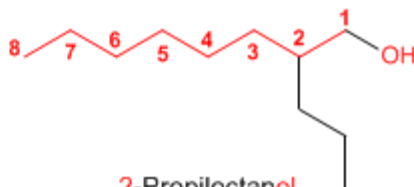
Regla 2. Se numera la cadena principal para que el grupo -OH tome el localizador más bajo. El grupo hidroxilo tiene preferencia sobre cadenas carbonadas, halógenos, dobles y triples enlaces.



Regla 3. El nombre del alcohol se construye cambiando la terminación -o del alcano con igual número de carbonos por -ol.

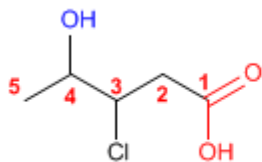


3-Etilheptanol

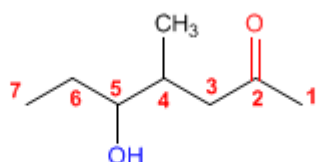


2-Propiloctanol

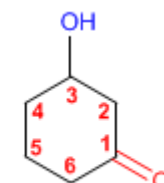
Regla 4. Cuando en la molécula hay grupos funcionales de mayor prioridad, el alcohol pasa a ser un mero sustituyente y se llama **hidroxi-**. Son prioritarios frente a los alcoholes: ácidos carboxílicos, anhídridos, ésteres, haluros de alcanoilo, amidas, nitrilos, aldehídos y cetonas.



Ácido 3-cloro-4-hidroxipentanoico

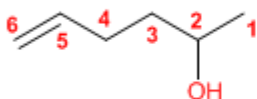


5-Hidroxi-4-metilheptanona

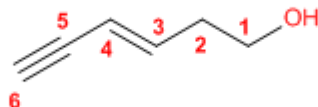


3-Hidroxiciclohexanona

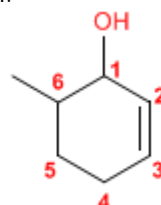
Regla 5. El grupo -OH es prioritario frente a los alquenos y alquinos. La numeración otorga el localizador más bajo al -OH y el nombre de la molécula termina en -ol.



Hex-5-en-2-ol



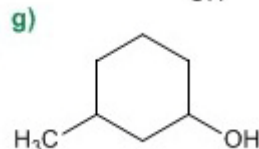
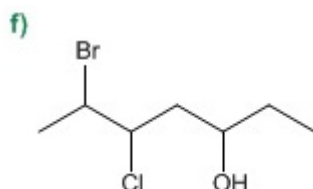
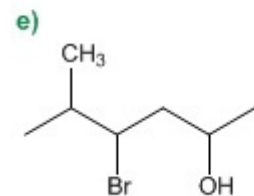
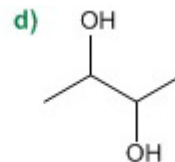
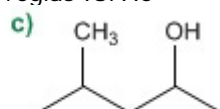
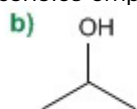
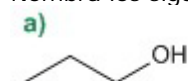
Hex-3-en-5-in-1-ol



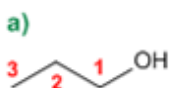
6-Metilciclohex-2-en-1-ol

Nomenclatura de Alcoholes - Problema 0.1

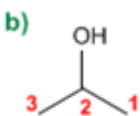
Nombra los siguientes alcoholes empleando reglas IUPAC



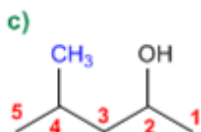
Solución:



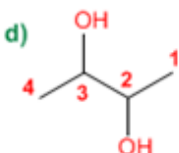
1. Cadena principal: la de mayor longitud que contenga el -OH (propano)
2. Numeración: otorga al -OH el localizador más bajo.
3. Sustituyentes: no
4. Nombre: Propan-1-ol



1. Cadena principal: la de mayor longitud que contenga el -OH (propano)
2. Numeración: indiferente.
3. Sustituyentes: no
4. Nombre: Propan-2-ol



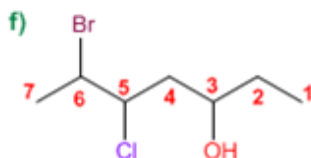
1. Cadena principal: la de mayor longitud que contenga el -OH (pentano)
2. Numeración: otorga al -OH el localizador más bajo (-OH preferente sobre cadenas)
3. Sustituyentes: metilo en 4
4. Nombre: 4-Metilpentan-2-ol



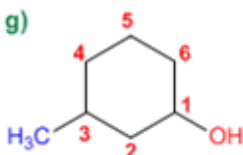
1. Cadena principal: mayor longitud (butano)
2. Numeración: comienza en uno de los extremos.
3. Sustituyentes: no
4. Nombre: Butano-2,3-diol



1. Cadena principal: mayor longitud (hexano)
2. Numeración: comienza en el extremo derecho, para otorgar al -OH el localizador más bajo.
3. Sustituyentes: bromo en posición 4 y metilo en 5.
4. Nombre: 4-Bromo-5-metilhexan-2-ol



1. Cadena principal: mayor longitud (heptano)
2. Numeración: comienza en extremo que otorga el localizador más bajo al -OH.
3. Sustituyentes: bromo en 6 y cloro en 5.
4. Nombre: 6-Bromo-5-cloroheptan-3-ol



1. Cadena principal: ciclo de seis miembros (ciclohexano)
2. Numeración: comienza en el carbono del -OH.
3. Sustituyentes: metilo en 3.
4. Nombre: 3-Metilciclohexanol

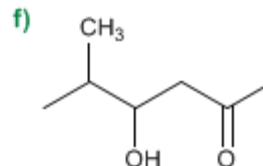
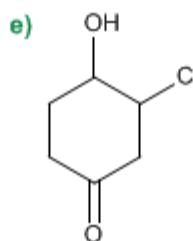
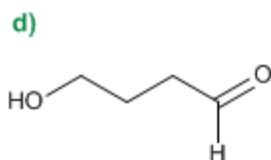
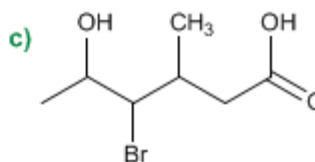
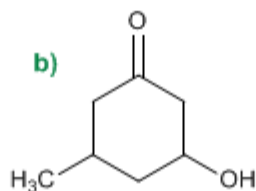
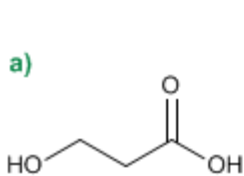
1. Cuando en una molécula hay más de un grupo -OH se pueden emplear los prefijos de cantidad di, tri, tetra, penta, hexa,..... La numeración debe otorgar los menores localizadores a los -OH.

2. El nombre del alcohol se construye comenzando por los sustituyentes, precedidos por sus respectivos localizadores, terminando en el nombre de la cadena principal. La terminación -o del alcano correspondiente se sustituye por -ol.

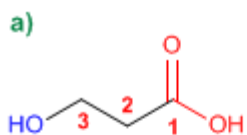
3. En el caso de alcoholes cíclicos no es necesario indicar la posición del grupo hidroxilo, puesto que siempre toma localizador 1.

Nomenclatura de Alcoholes - Problema 0.2

Nombra los siguientes moléculas, en las que el alcohol actúa como sustituyente.



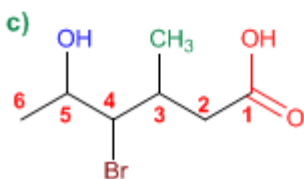
Solución



1. Cadena principal: más larga que contenga el grupo funcional (propano)
2. Grupo funcional: ácido carboxílico
3. Numeración: localizador más bajo al grupo ácido
4. Sustituyentes: grupo **hidroxi** en 3.
5. Nombre: **Acido 3-hidroxi**propanoico



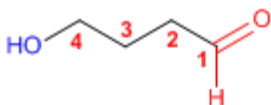
1. Cadena principal: ciclo de seis miembros (ciclohexano)
2. Grupo funcional: cetona
3. Numeración: localizador más bajo al grupo carbonilo
4. Sustituyentes: grupo **hidroxi** en 3 y **metilo** en 4.
5. Nombre: **2-Hidroxi-5-metilciclohexanona**



1. Cadena principal: más larga que contenga el grupo funcional (hexano)
2. Grupo funcional: ácido carboxílico
3. Numeración: asigna el localizador más bajo al grupo ácido.
4. Sustituyentes: **bromo** en 4, grupo **hidroxi** en 5 y **metilo** en 3
5. Nombre: **Acido 4-bromo-6-hidroxi-3-metilhexanoico**

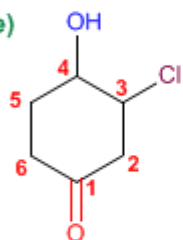
Los ácidos carboxílicos y las cetonas son prioritarios sobre los alcoholes.
El alcohol pasa a ser un sustituyente más de la molécula, ordenándose alfabéticamente con el resto de sustituyentes.

d)



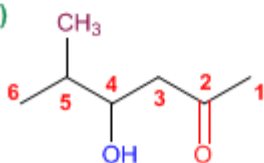
1. Cadena principal: más larga que contenga el grupo funcional (butano)
2. Grupo funcional: aldehído
3. Numeración: localizador más bajo al grupo carbonilo
4. Sustituyentes: grupo **hidroxi** en 4.
5. Nombre: **4-Hidroxibutanal**

e)



1. Cadena principal: ciclo de seis miembros
2. Grupo funcional: cetona
3. Numeración: localizador más bajo al carbonilo
4. Sustituyentes: **cloro** en 3 e **hidroxi** en 4.
5. Nombre: **3-Cloro-4-hidroxiciclohexanona**

f)



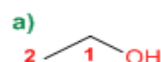
1. Cadena principal: más larga que contenga el grupo funcional (propano)
2. Grupo funcional: cetona
3. Numeración: localizador más bajo al grupo carbonilo
4. Sustituyentes: grupo **hidroxi** en 4 y **metilo** en 5.
5. Nombre: **3-Hidroxi-4-metilhexan-2-ona**

Nomenclatura de Alcoholes - Problema 0.3

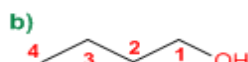
Dibujar la estructura de los siguientes alcoholes:

- | | |
|--------------------------|-----------------------------------|
| a) Etanol | i) Ciclopent-2-enol |
| b) Butanol | j) 2,3-Dimetilciclohexanol |
| c) 2-Metilpropan-1-ol | k) Octa-3,5-dien-2-ol |
| d) 2-Metilbutan-2-ol | l) Hex-4-en-1-in-3-ol |
| e) 3-Metilbutan-2-ol | m) 2-Bromohept-2-en-1,4-diol |
| f) 3-Metilbutan-1-ol | n) 2-Fenil-5-metilheptan-2-ol |
| g) 2,3-Pentanodiol | o) Alcohol bencílico |
| h) 2-Etil-pent-3-en-1-ol | p) 1,2,3-Propanotriol (glicerina) |

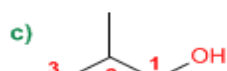
Solución:



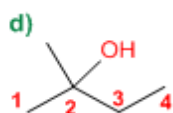
Etanol



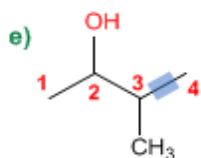
Butanol



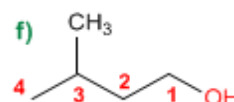
2-Metilpropan-1-ol



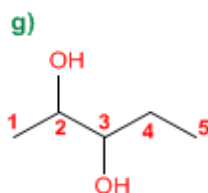
2-Metilbutan-2-ol



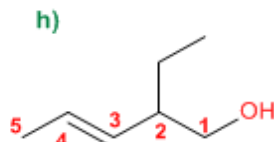
3-Metilbutan-2-ol



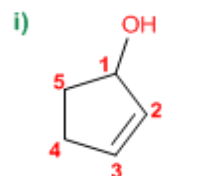
3-Metilbutan-1-ol



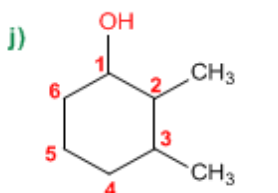
2,3-Pentanodiol



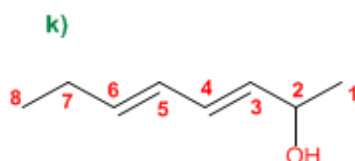
2-Etil-pent-3-en-1-ol



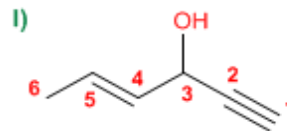
Ciclopent-2-enol



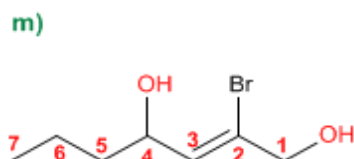
2,3-Dimetilciclohexanol



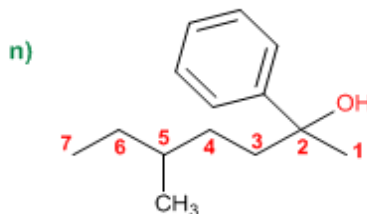
Octa-3,5-dien-2-ol



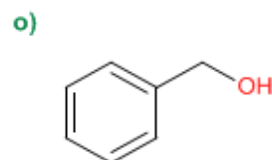
Hex-4-en-1-in-3-ol



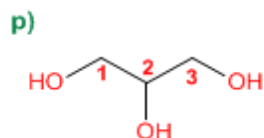
2-Bromohept-2-en-1,4-diol



2-Fenil-5-metilheptan-2-ol



Alcohol bencílico

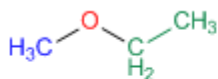


1,2,3-Propanotriol (glicerina)

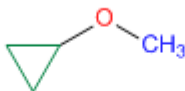
TEORÍA DE ÉTERES

Nomenclatura de éteres - epóxidos

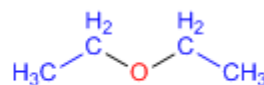
La nomenclatura de los éteres consiste en nombrar alfabéticamente los dos grupos alquilo que parten del oxígeno, terminando el nombre en éter. Veamos algunos ejemplos:



Etil metil éter

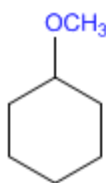


Ciclopropil metil éter

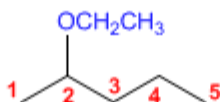


Dietil éter

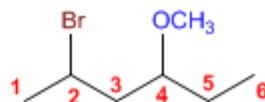
También se pueden nombrar los éteres como grupos alcoxi.



Metóxiciclohexano



2-Etoxi pentano

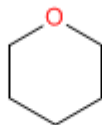


2-Bromo-4-metoxihexano

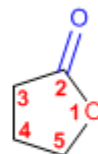
Los éteres cíclicos se forman sustituyendo $-CH_2-$ del ciclo por $-O-$. Este cambio se indica con el prefijo **oxa-**.



Oxaciclopropano



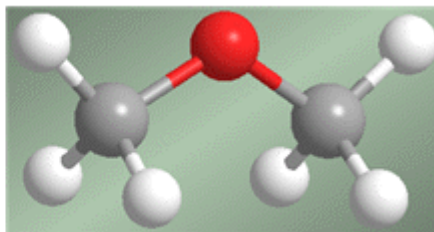
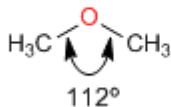
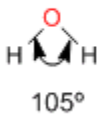
Oxaciclohexano



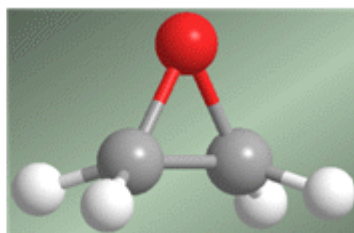
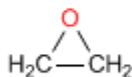
2-oxo-oxaciclopentano

Estructura y enlace en éteres y epóxidos

Los éteres son moléculas de estructura similar al agua y alcoholes. El ángulo entre los enlaces C-O-C es mayor que en el agua debido a las repulsiones estéricas entre grupos voluminosos.

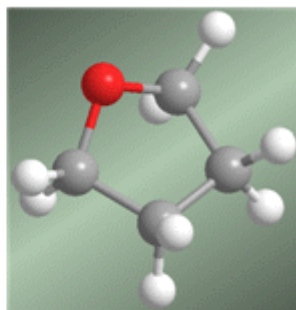
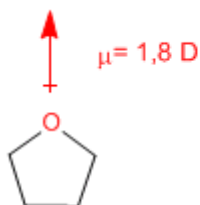


En el caso de los epóxidos la característica más relevante es la tensión del anillo, debida a ángulos de enlace muy distantes a los 109°.



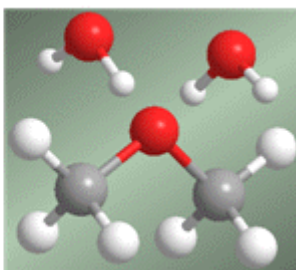
El enlace C-O-C presenta un ángulo de 61°.

Los éteres son moléculas muy polares. Así, el Dietil éter presenta un momento dipolar de 1,2 D. Este momento dipolar es aún más importante en éteres cíclicos (oxaciclopropano, tetrahydrofurano) que presentan momentos dipolares sobre 1,8 D, similares al agua.





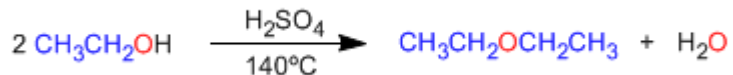
Solubilidad agua = 7,5 g/100ml



Síntesis de éteres por condensación de alcoholes

1. Éteres a partir de alcoholes primarios

Los éteres simétricos pueden prepararse por condensación de alcoholes. La reacción se realiza bajo calefacción (140°C) y con catálisis ácida. Así, dos moléculas de etanol condensan para formar dietil éter.

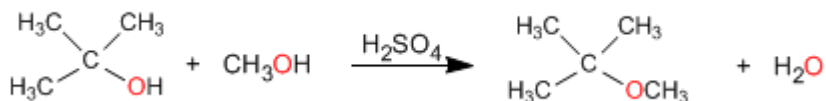


El mecanismo de la reacción transcurre en las siguientes etapas:



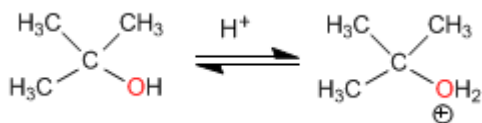
2. Uno de los alcoholes es secundario o terciario

En este caso la reacción transcurre en condiciones más suaves, a través de mecanismos $\text{S}_{\text{N}}1$.

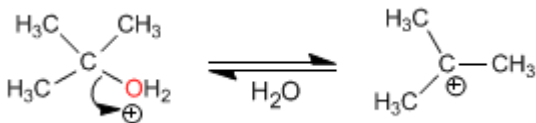


El mecanismo transcurre con formación de un carbocatión terciario de gran estabilidad

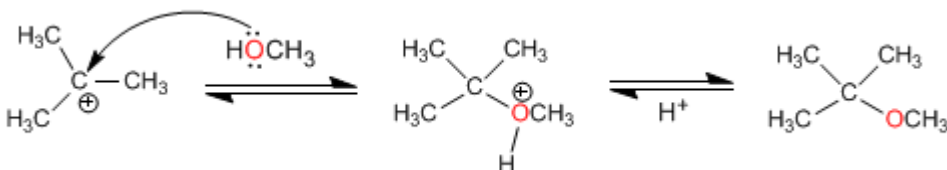
Etapa 1. Protonación del alcohol terciario



Etapa 2. Formación del carbocatión por pérdida de agua

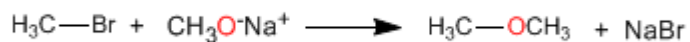


Etapa 3. Ataque nucleófilo del metanol



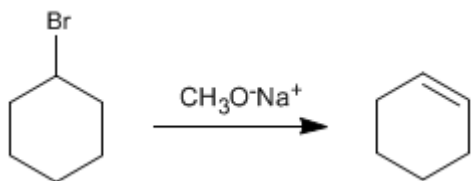
Síntesis de Williamson de los éteres

La reacción entre un haloalcano primario y un alcóxido (o bien alcohol en medio básico) es el método más importante para preparar éteres. Esta reacción es conocida como síntesis de Williamson.

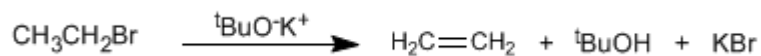


Esta reacción transcurre a través del mecanismo $\text{S}_{\text{N}}2$.

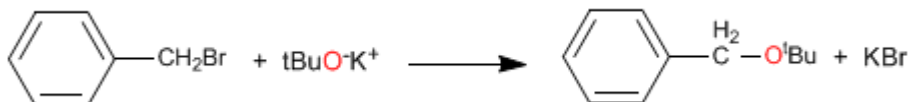
La importante basicidad de los alcóxidos produce reacciones de eliminación con sustratos secundarios y terciarios, formando alquenos en lugar de éteres.



Otra situación en la que Williamson no rinde éteres, es en el caso de emplear alcóxidos impedidos, como *tert*-butóxido de potasio. Debido a su gran tamaño el *tert*-butóxido elimina incluso con sustratos primarios.



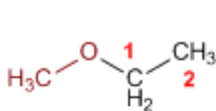
Con haloalcanos primarios y sobre todo con haloalcanos que carecen de hidrógenos β el rendimiento de Williamson es muy bueno.



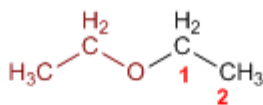
PROBLEMAS NOMENCLATURA - ÉTERES

Nomenclatura de Éteres - Reglas IUPAC

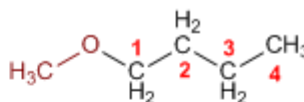
Regla 1. Los éteres pueden nombrarse como alcoxi derivados de alcanos (nomenclatura IUPAC sustitutiva). Se toma como cadena principal la de mayor longitud y se nombra el alcóxido como un sustituyente.



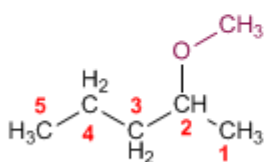
Metoxietano



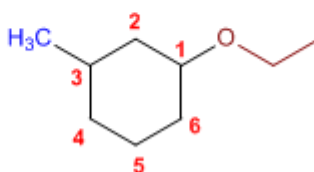
Etoxietano



1-Metoxibutano

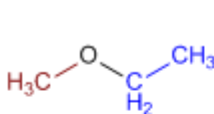


2-Metoxipentano

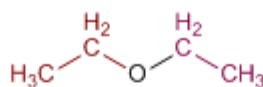


1-Etoxi-3-metilciclohexano

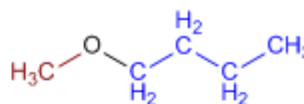
Regla 2. La nomenclatura funcional (IUPAC) nombra los éteres como derivados de dos grupos alquilo, ordenados alfabéticamente, terminando el nombre en la palabra éter.



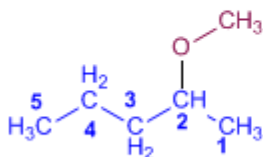
Etil metil éter



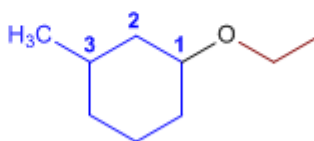
Dietil éter



Butil metil éter



Metil pent-2-il éter



Etil 3-metilciclohexil éter

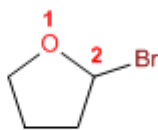
Regla 3. Los éteres cíclicos se forman sustituyendo un $-\text{CH}_2-$ por $-\text{O}-$ en un ciclo. La numeración comienza en el oxígeno y se nombran con el prefijo oxa- seguido del nombre del ciclo.



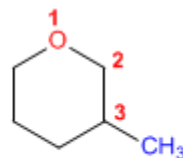
Oxaciclopropano



Oxaciclobutano



2-Bromooxaciclopentano

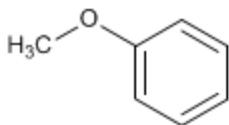


3-Metiloxaciclohexano

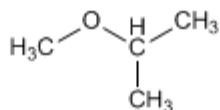
Nomenclatura de Éteres - Problema 0.1

Nombra los siguientes éteres:

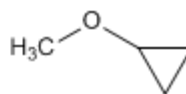
a)



b)



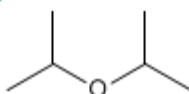
c)



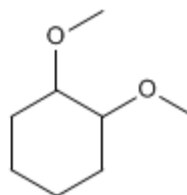
d)



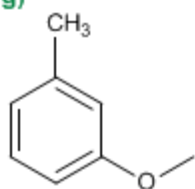
e)



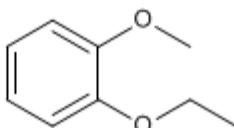
f)



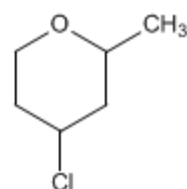
g)



h)

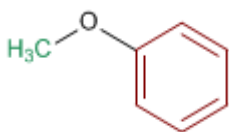


i)



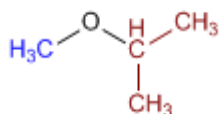
Solución:

a)



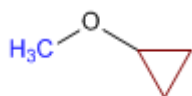
1. Sustituyentes: **fenil** y **metil**
2. Nombre: **Fenil metil** éter

b)



1. Sustituyentes: **isopropil** y **metil**
2. Nombre: **Isopropil metil** éter

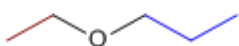
c)



1. Sustituyentes: **ciclopropil** y **metil**
2. Nombre: **Ciclopropil metil** éter

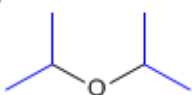
El nombre de los éteres se construye terminando en la palabra éter el nombre de las cadenas que parten del oxígeno. Estas cadenas se nombran como sustituyentes y se ordenan alfabéticamente. Obsérvese el espacio de separación entre las palabras.

d)



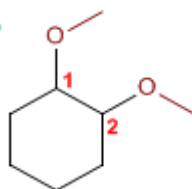
1. Sustituyentes: **etilo** y **propilo**
2. Nombre: **Etil propil** éter

e)



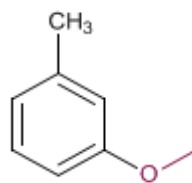
1. Sustituyentes: **isopropilos**
2. Nombre: **Diisopropil** éter

f)



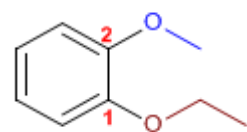
1. Cadena principal: ciclo de seis miembros (ciclohexano)
2. Numeración: otorga localizadores más bajos a sustituyentes
3. Sustituyentes: **metoxidos** en 1,2
4. Nombre: **1,2-Dimetoxiciclohexano**

g)



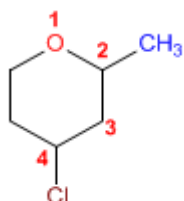
1. Cadena principal: Tolueno
2. Numeración: metilo y metóxido en meta.
3. Sustituyentes: **metoxido**
4. Nombre: **m-Metoxitolueno**

h)



1. Cadena principal: Benceno
2. Numeración: Comienza en el etoxi (antes alfabéticamente)
3. Sustituyentes: **etoxido** en 1 y **metoxido** en 2. (posición meta)
4. Nombre: **m-Etoximetoxibenceno**

i)



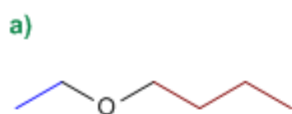
1. Cadena principal: ciclo de 6 miembros (oxaciclohexano)
2. Numeración: comienza en el oxígeno, prosigue a la derecha para otorgar a los sustituyentes los menores localizadores.
3. Sustituyentes: **cloro** y **metilo**
4. Nombre: **4-Cloro-2-metiloxa**ciclohexano

Nomenclatura de Éteres - Problema 0.2

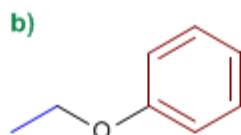
Dibuja las estructuras de los siguientes éteres:

- | | |
|--------------------------|----------------------------------|
| a) Butil etil éter | k) 2-Clorofenil fenil éter |
| b) Etil fenil éter | l) tert-butil isopropil éter |
| c) Difenil éter | m) 2-Metoxi-3-fenilbutan-1-ol |
| d) Divinil éter | n) Dietil éter |
| e) Isopropoxibutano | o) m-Etoxifenol |
| f) Bencil fenil éter | p) 2,3-Dimetiloxaciclopropano |
| g) Metoxiciclohexano | q) 3-Metoxioxaciclohexano |
| h) 4-Metoxipent-2-eno | r) 2-Etil-3-metiloxaciclopentano |
| i) 4-Etoxibut-1-ino | s) Ciclohexil ciclopropil éter |
| j) Ciclohexil fenil éter | t) 2-Metoxipentano |

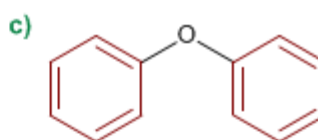
Solución



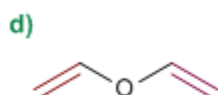
Butil etil éter



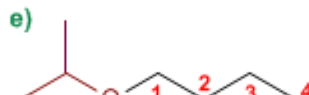
Etil fenil éter



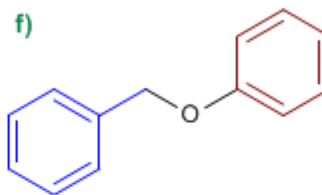
Difenil éter



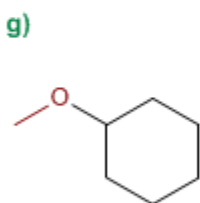
Divinil éter



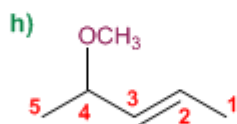
1-Isopropoxibutano



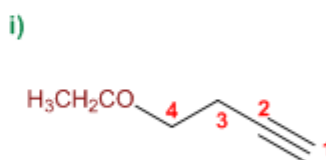
Bencil fenil éter



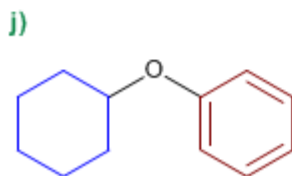
Metoxiciclohexano



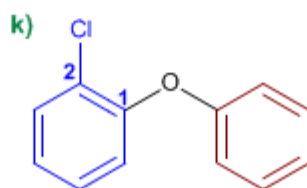
4-Metoxipent-2-eno



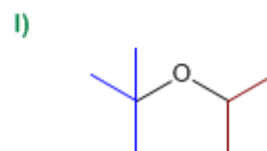
4-Etoxibut-1-ino



Ciclohexil fenil éter

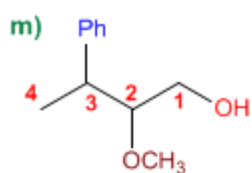


2-Clorofenil fenil éter

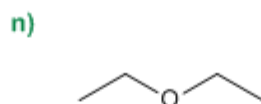


tert-butil isopropil éter

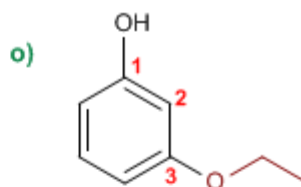
Los grupos alcóxido (metóxido, etóxido....) se ordenan alfabéticamente con los demás sustituyentes de la molécula y no tienen ninguna preferencia sobre ellos



2-Metoxi-3-fenilbutan-1-ol



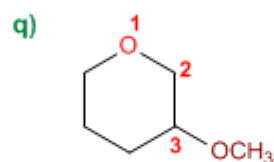
Dietil éter



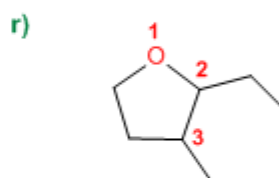
m-Etoxifenol



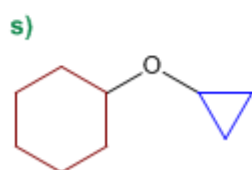
2,3-Dimetiloxa**c**ciclopropano



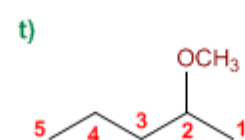
3-Metoxioxa**c**ciclohexano



2-Etil-3-metiloxa**c**ciclopentano



Ciclohexil ciclopropil éter

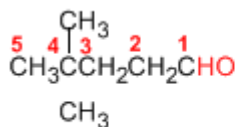


2-Metoxipentano

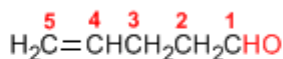
Nomenclatura de Aldehídos y Cetonas

Los aldehídos se nombran reemplazando la terminación **-ano** del alcano correspondiente por **-al**. No es necesario especificar la posición del grupo aldehído, puesto que ocupa el extremo de la cadena (localizador 1).

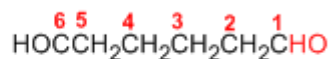
Cuando la cadena contiene dos funciones aldehído se emplea el sufijo **-dial**.



4,4-Dimetilpentanal

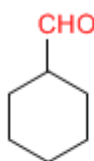


Hex-4-enal

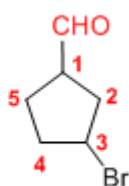


Pentanodial

El grupo **-CHO** unido a un ciclo se llama **-carbaldehído**. La numeración del ciclo se realiza dando localizador 1 al carbono del ciclo que contiene el grupo aldehído.



Ciclohexanocarbaldehído

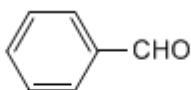


3-Bromociclopentanocarbaldehído

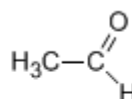
Algunos nombres comunes de aldehídos aceptados por la IUPAC son:



Formaldehído
(Metanal)

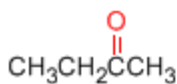


Benzaldehído
(Bencenocarbaldehído)

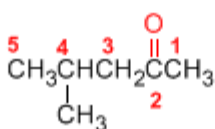


Acetaldehído
(Etanal)

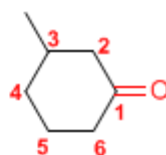
Las cetonas se nombran sustituyendo la terminación **-ano** del alcano con igual longitud de cadena por **-ona**. Se toma como cadena principal la de mayor longitud que contiene el grupo carbonilo y se numera para que éste tome el localizador más bajo.



Butanona

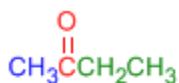


4-Metil-2-pentanona

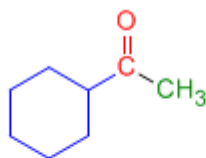


3-Metilciclohexanona

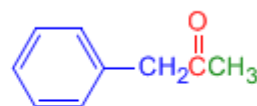
Existe un segundo tipo de nomenclatura para las cetonas, que consiste en nombrar las cadenas como sustituyentes, ordenándolas alfabéticamente y terminando el nombre con la palabra **cetona**.



Etil metil cetona



Ciclohexil metil cetona



Fenil metil cetona

[Siguiete >](#)

[\[Volver\]](#)

Charles Friedel (1832 - 1899)



Origen: Químico frances..

Lugar de nacimiento: Estrasburgo.

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

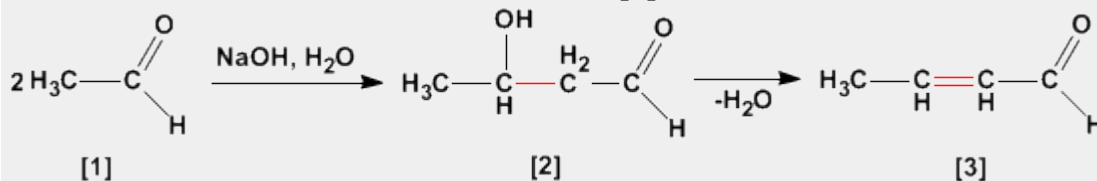
Docencia: Profesor en la Universidad de la Sorbona.

Investigación: Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

Premio Nobel:

Aldólica (Condensación)

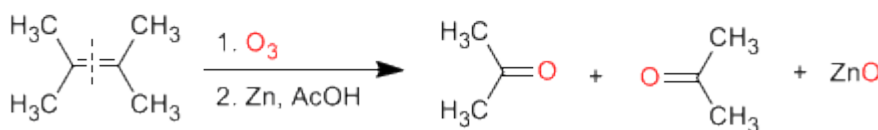
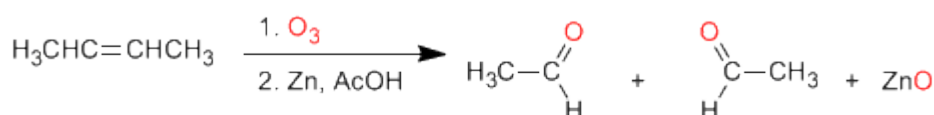
La condensación aldólica es una reacción de aldehídos o cetonas **[1]** que forma 3-hidroxicarbonilos (aldoles) **[2]**. El 3-hidroxialdehído **[2]** bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado **[3]**.



Preparación de aldehídos y cetonas

Los aldehídos y cetonas pueden ser preparados por oxidación de alcoholes, ozonólisis de alquenos, hidratación de alquinos y acilación de Friedel-Crafts como métodos de mayor importancia.

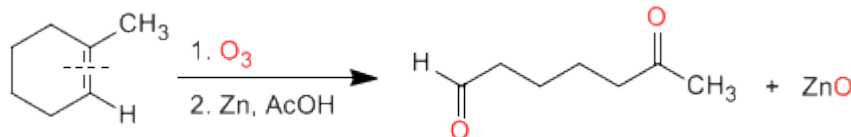
a) **Ozonólisis de alquenos:** Los alquenos rompen con ozono formando aldehídos y/o cetonas. Si el alqueno tiene hidrógenos vinílicos da aldehídos. Si tiene dos cadenas carbonadas forma cetonas.



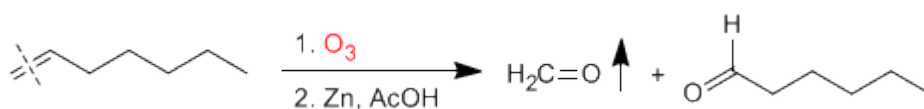
Ozonólisis

Los alquenos simétricos y terminales permiten la preparación de carbonilos mediante ozonólisis

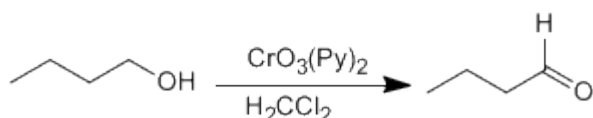
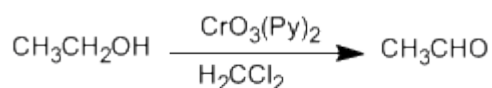
La ozonólisis de alquenos cíclicos produce compuestos dicarbonílicos:



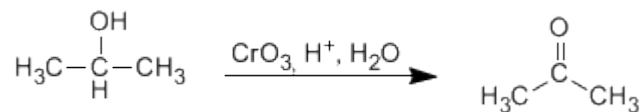
Los alquenos terminales rompen formando metanal, que separa fácilmente de la mezcla por su bajo punto de ebullición.



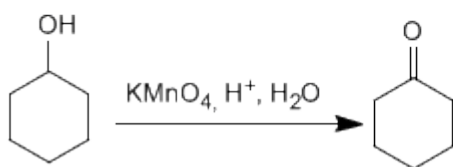
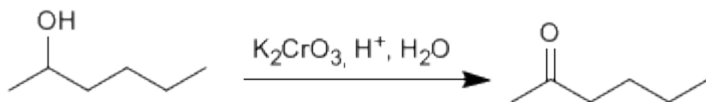
b) **Oxidación de alcoholes:** Los alcoholes primarios y secundarios se oxidan para dar aldehídos y cetonas respectivamente. Deben tomarse precauciones en la oxidación de alcoholes primarios, puesto que sobreoxidan a ácidos carboxílicos en presencia de oxidantes que contengan agua. En estos caso debe trabajarse con reactivos anhidros, como el clorocromato de piridino en diclorometano (PCC), a temperatura ambiente.



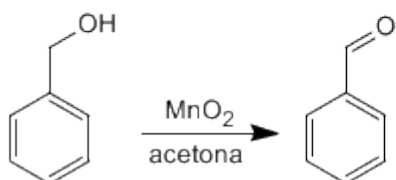
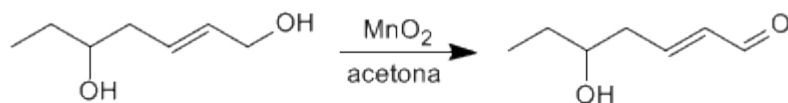
Los alcoholes secundarios dan cetonas por oxidación. Se emplean como oxidantes permanganato, dicromato, trióxido de cromo.



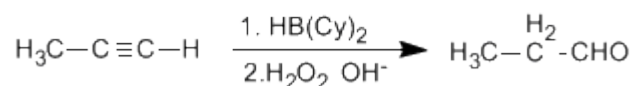
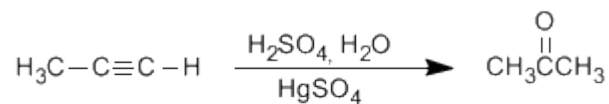
La oxidación supone la pérdida de dos hidrógenos del alcohol. Los alcoholes terciarios no pueden oxidar puesto que carecen de hidrógeno sobre el carbono.



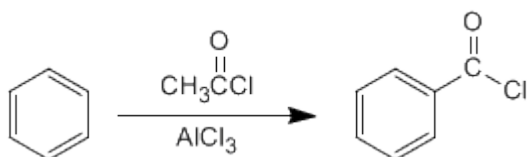
Los alcoholes alílicos y bencílicos se transforman en aldehídos o cetonas por oxidación con dióxido de manganeso en acetona. Esta reacción tiene una elevada selectividad y no oxida alcoholes que no se encuentren en dichas posiciones.



c) **Hidratación de alquinos:** Los alquinos se pueden hidratar Markovnikov, formando cetonas, o bien antiMarkovnikov, para formar aldehídos.



d) **Acilación de Friedel-Crafts:** La introducción de grupos acilo en el benceno permite la preparación de cetonas con cadenas aromáticas.



Otto Paul Hermann Diels (1876 - 1954)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

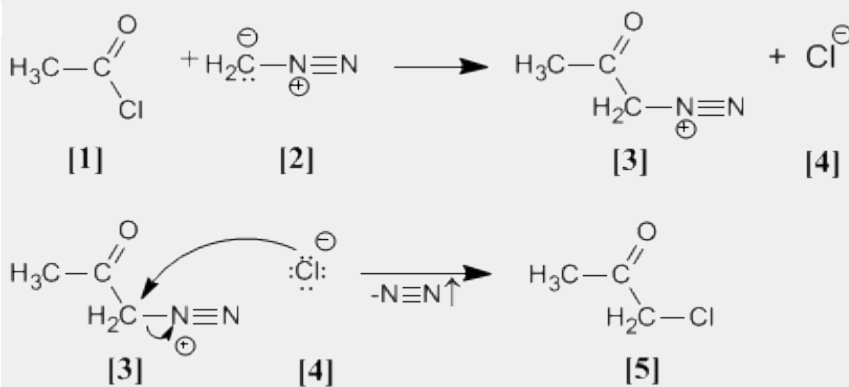
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Premio Nobel: En 1950 recibió el Premio Nobel junto a Kurt Alder

Arndt Eistert (Síntesis)

Cloruro de acetilo [1] se trata con diazometano [2] rindiendo la sal de diazonio [3]. El cloruro [4] producido reacciona con la sal de diazonio para dar la α -clorocetona [5].

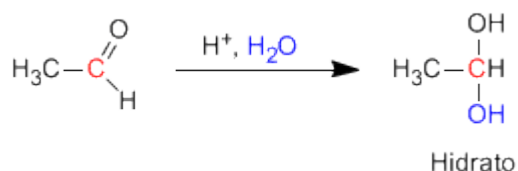


Síntesis de Arndt Eistert

Esta reacción permite transformar haluros de alcanoilo en cetonas halogenadas en su posición alfa.

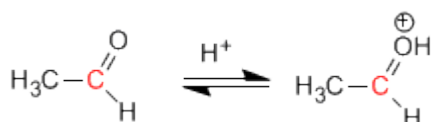
Formación de Hidratos

Los aldehídos y cetonas reaccionan en medio ácido acuoso para formar hidratos. El mecanismo consta de tres etapas. La primera y más rápida consiste en la protonación del oxígeno carbonílico. Esta protonación produce un aumento de la polaridad sobre el carbono y favorece el ataque del nucleófilo. En la segunda etapa el agua ataca al carbono carbonilo, es la etapa lenta del mecanismo. En la tercera etapa se produce la desprotonación del oxígeno formándose el hidrato final.

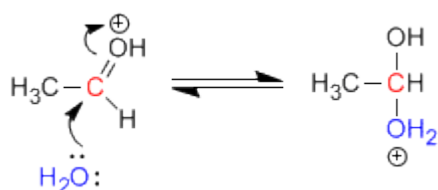


Mecanismo de la reacción

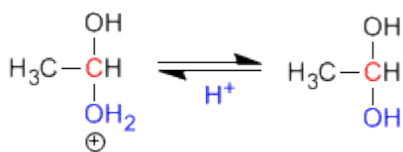
Etapa 1. Protonación del oxígeno carbonílico.



Etapa 2. Ataque nucleófilo del agua al carbonilo protonado.



Etapa 3. Desprotonación del hidrato





Origen: Químico estadounidense.

Lugar de nacimiento: Budapest

Formación: Se doctoró en la Universidad de Budapest en 1949

Docencia: Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

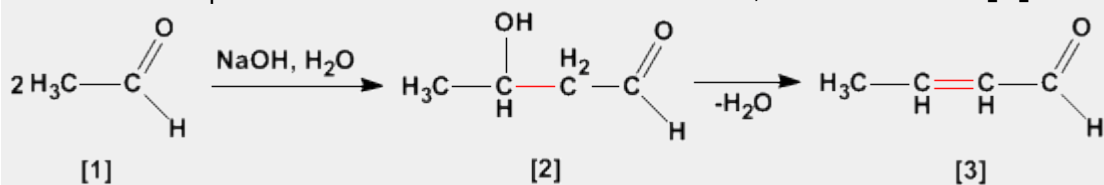
Industria: Trabajó en los laboratorios de la Dow Chemical de Ontario

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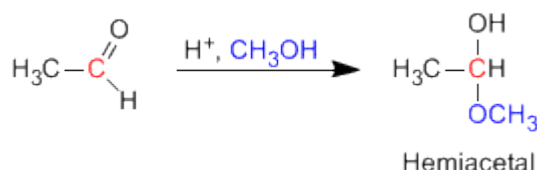
Aldólica (Condensación)

La condensación aldólica es una reacción de aldehídos o cetonas **[1]** que forma 3-hidroxicarbonilos (aldoles) **[2]**. El 3-hidroxialdehído **[2]** bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado **[3]**.



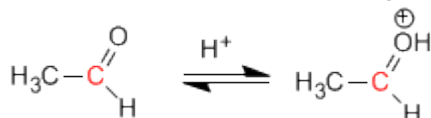
Formación de Hemiacetales

Los hemiacetales se forman por reacción de un equivalente de alcohol con el grupo carbonilo de un aldehído o cetona. Esta reacción se cataliza con ácido y es equivalente a la formación de hidratos.

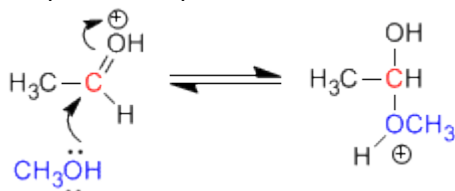


Mecanismo de la reacción:

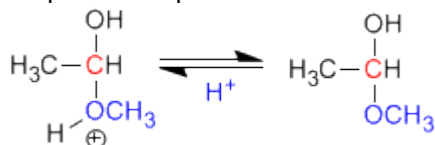
Etapas 1. Protonación del oxígeno carbonílico.



Etapas 2. Ataque nucleófilo del metanol al carbonilo protonado.



Etapas 3. Desprotonación del hemiacetal



Otto Paul Hermann Diels (1876 - 1954)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

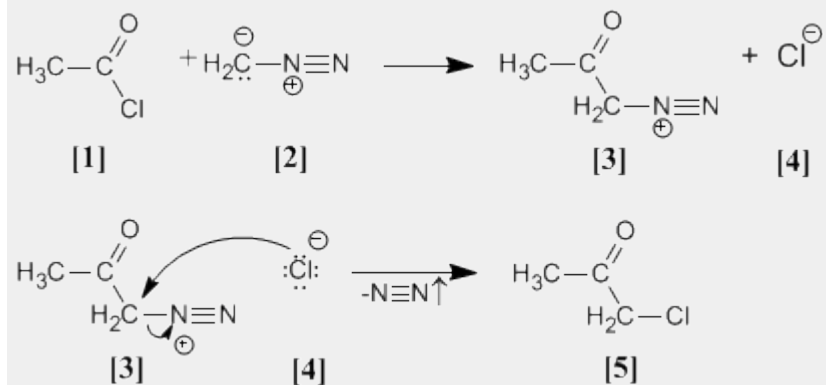
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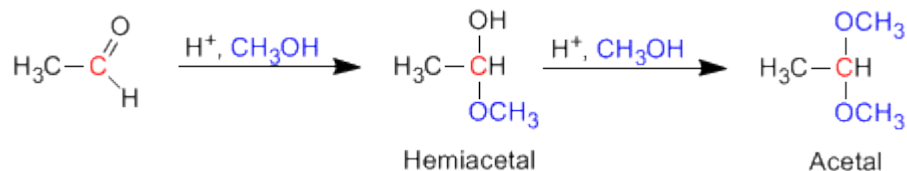
Arndt Eistert (Síntesis)

Cloruro de acetilo **[1]** se trata con diazometano **[2]** rindiendo la sal de diazonio **[3]**. El cloruro **[4]** producido reacciona con la sal de diazonio para dar la α -clorocetona **[5]**.



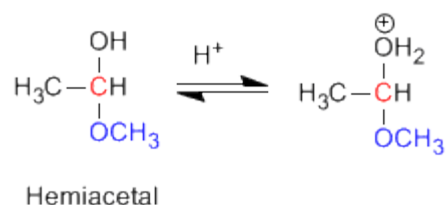
Formación de Acetales

Los aldehídos y cetonas reaccionan con alcoholes bajo condiciones de catálisis ácida, formando en una primera etapa hemiacetales, que posteriormene evolucionan por reacción con un segundo equivalente de alcohol a acetales.

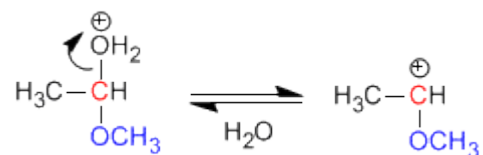


Mecanismo para la formación de acetales

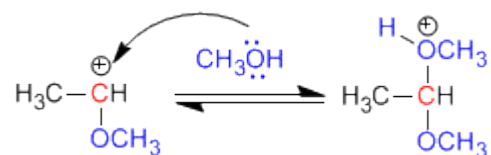
Etapa 1. Protonación del grupo hidroxilo



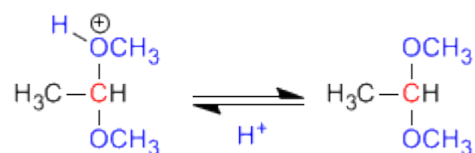
Etapa 2. Pérdida de agua.



Etapa 3. Ataque del alcohol al carbocatión



Etapa 4. Desprotonación del acetal



Otto Paul Hermann Diels (1876 - 1954)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

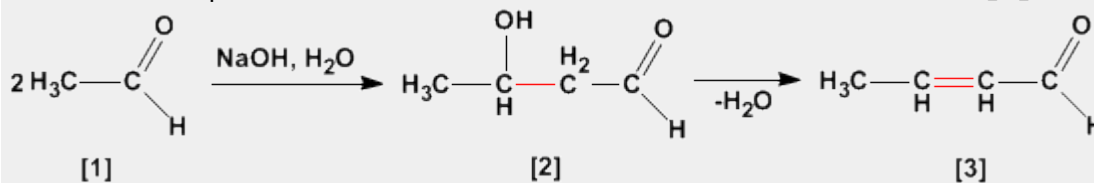
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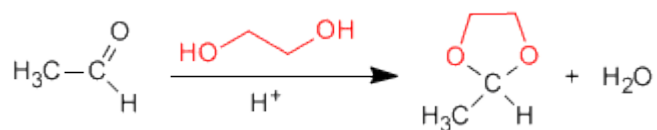
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La condensación aldólica es una reacción de aldehídos o cetonas **[1]** que forma 3-hidroxicarbonilos (aldoles) **[2]**. El 3-hidroxialdehído **[2]** bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado **[3]**.



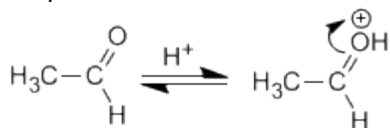
Formación de acetales cíclicos

Los 1,2- y 1,3-dioles reaccionan con aldehídos y cetonas formando acetales cíclicos. Los equilibrios se desplazan hacia el producto final eliminando el agua formada por destilación azeotrópica con benceno o tolueno.

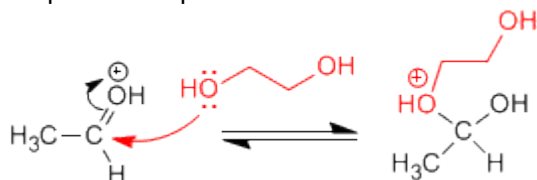


Mecanismo para la formación de acetales cíclicos:

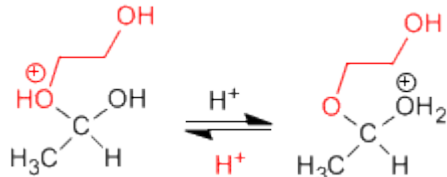
Etapa 1. Protonación del carbonilo



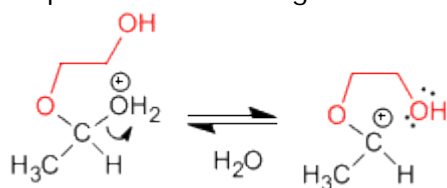
Etapa 2. Ataque nucleófilo del diol al carbonilo.



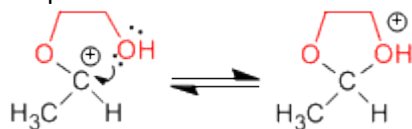
Etapa 3. Equilibrio ácido base entre el éter y el alcohol



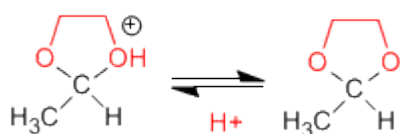
Etapa 4. Pérdida de agua



Etapa 5. Ciclación



Etapa 6. Desprotonación del acetal cíclico



Kurt Alder (1902 - 1958)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

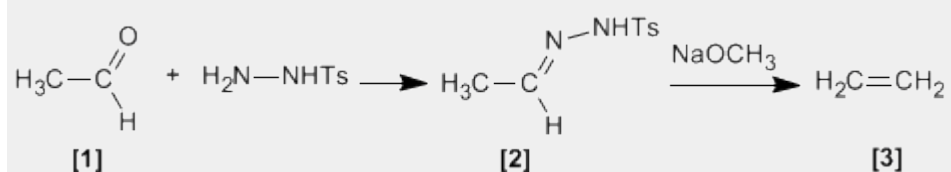
Docencia: Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

Investigación: Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos. Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

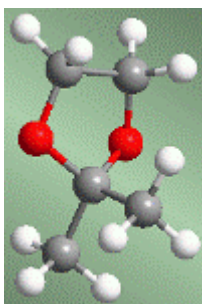
Premio Nobel: En 1950 recibió el Premio Nobel junto a Diels

Bamford Stevens (Reacción)

Tosilhidrazonas [2] de aldehídos o cetonas alifáticos [1] reaccionan con bases fuertes para dar alquenos [3].

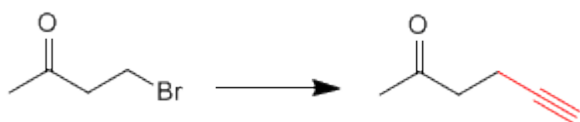


Acetales como grupos protectores

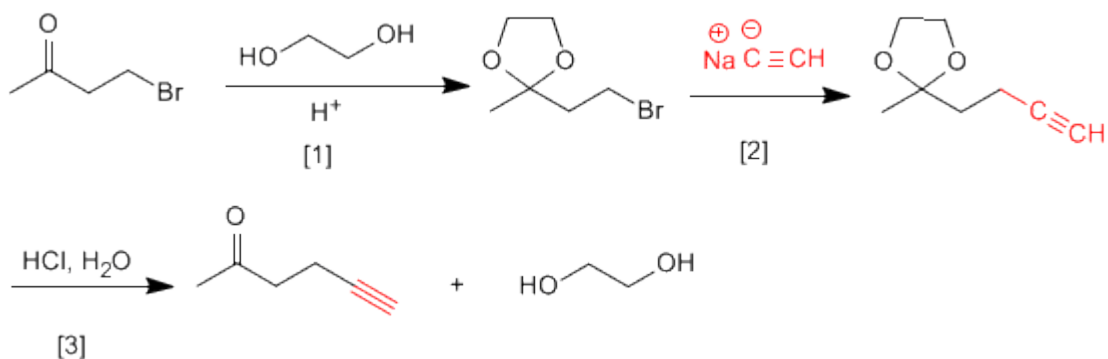


Los acetales pueden emplearse, por su estabilidad, como grupos protectores del carbonilo. El acetal es un éter, muy estable en medios básicos, aunque rompe en presencia de medios ácidos. En muchos procesos de síntesis el grupo carbonilo es incompatible con el reactivo utilizado. En estos casos debe protegerse para evitar que reaccione. La inestabilidad del acetal en medio ácido puede emplearse para desproteger el carbonilo.

Veamos algunos ejemplos:



Esta transformación requiere una sustitución, empleando como nucleófilo un acetiluro de sodio. El nucleófilo puede atacar también al grupo carbonilo, para evitarlo vamos a protegerlo.

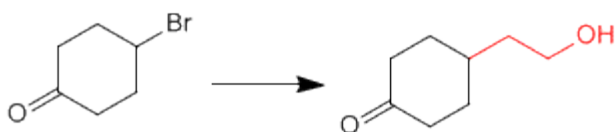


[1] Protección de la cetona.

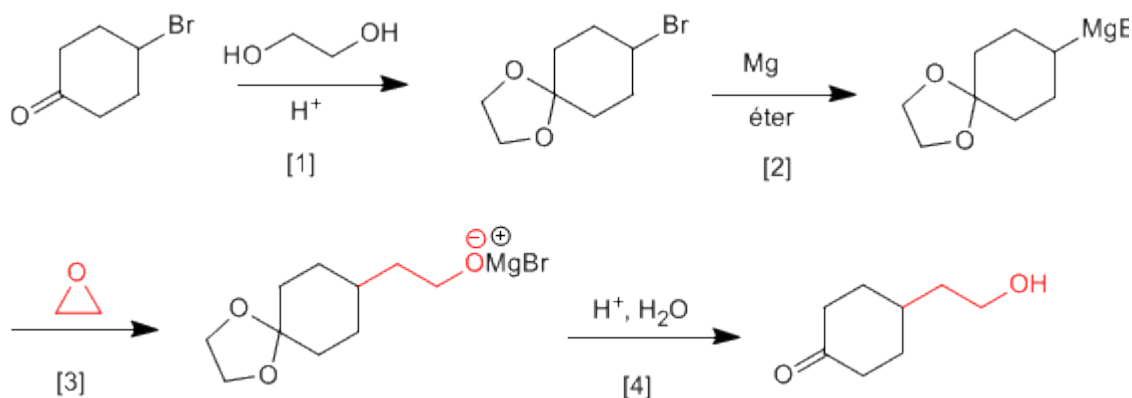
[2] Ataque del acetiluro al carbono del bromo.

[3] Desprotección del carbonilo

Veamos un segundo ejemplo:



Es necesario proteger la cetona antes de formar el organometálico para evitar la dimerización del compuesto.



- [1] Protección de la cetona.
 [2] Formación del magnesiano.
 [3] Apertura del oxaciclopropano.
 [4] Desprotección y protonación del alcóxido.

Otto Paul Hermann Diels (1876 - 1954)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

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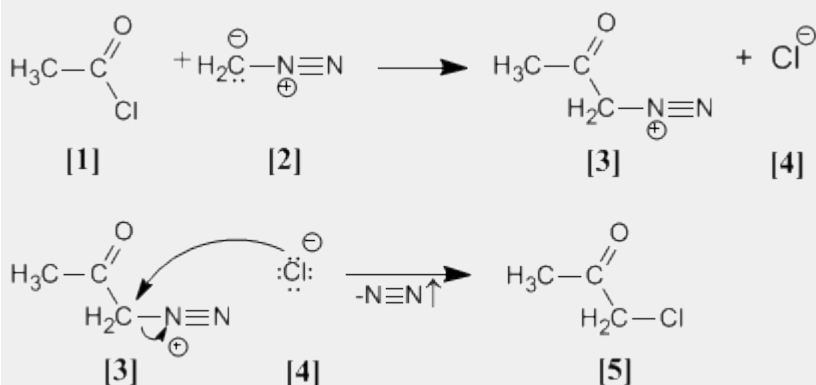
Investigación: En 1906 descubrió el anhídrido malónico.

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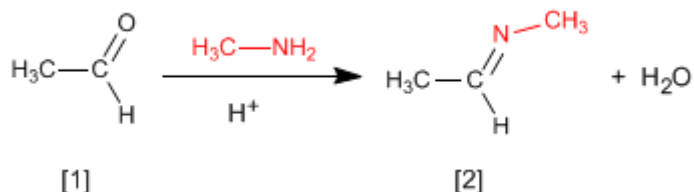
Arndt Eistert (Síntesis)

Cloruro de acetilo **[1]** se trata con diazometano **[2]** rindiendo la sal de diazonio **[3]**. El cloruro **[4]** producido reacciona con la sal de diazonio para dar la α-clorocetona **[5]**.



Formación de Iminas

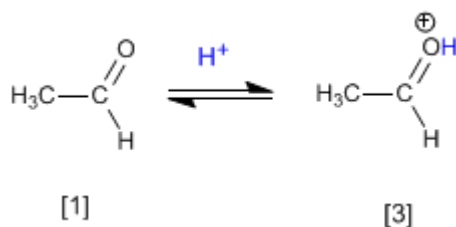
La reacción de aldehídos o cetonas **[1]** con aminas primarias genera iminas **[2]**. La reacción se favorece en un medio ligeramente ácido (pH=4.5).



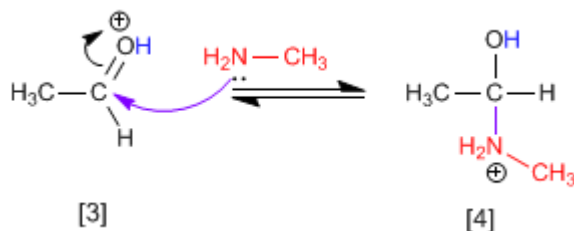
El control del pH es fundamental, puesto que se requiere la protonación del oxígeno del carbonilo para favorecer el ataque nucleófilo.

Mecanismo:

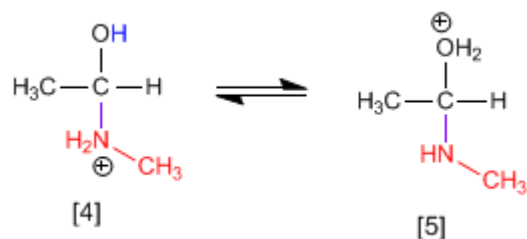
Etapas 1. Protonación del grupo carbonilo que aumenta la polaridad positiva sobre el carbono y favorece el ataque nucleófilo.



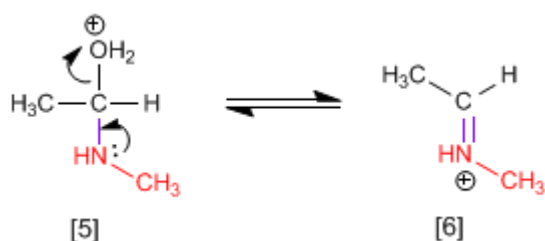
Etapas 2. Ataque nucleófilo de la amina primaria al carbono carbonilo.



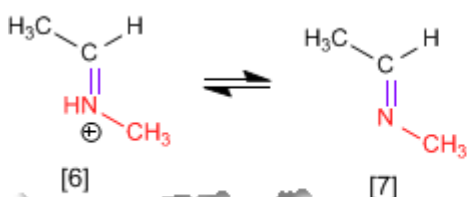
Etapas 3. Protonación del grupo hidroxilo para transformarlo en buen grupo saliente.



Etapas 4. Pérdida de agua y formación de la imina protonada.



Etapa 5. Desprotonación del catión.



George A. Olah (1927 -)



Origen: Químico estadounidense.

Lugar de nacimiento: Budapest

Formación: Se doctoró en la Universidad de Budapest en 1949

Docencia: Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

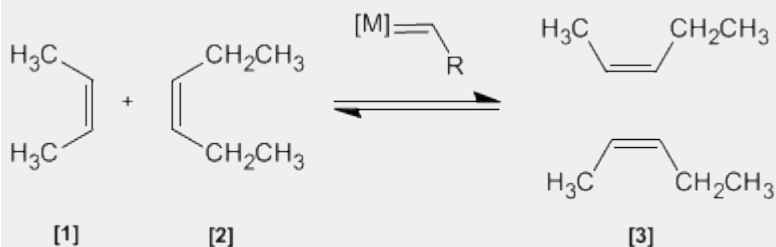
Industria: Trabajó en los laboratorios de la Dow Chemical de Ontario

Investigación: Olah consiguió preparar carbocationes estables utilizando componentes extremadamente ácidos.

Premio Nobel: En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

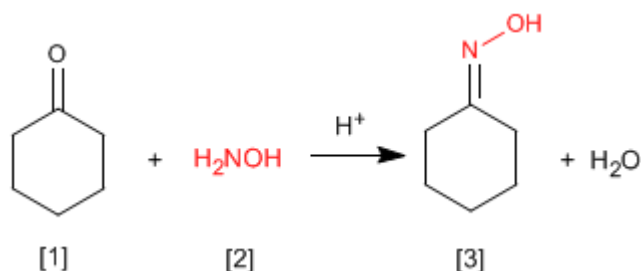
Metátesis de Alquenos

En esta reacción dos alquenos **[1]** y **[2]** son tratados con un metal de transición que actúa como catalizador, dando una mezcla de alquenos **[3]** (incluyendo isómeros Z/E). Este productos se obtiene por intercambio de grupos alquilideno.

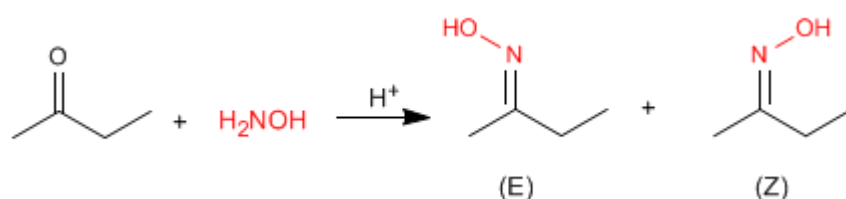


Formación de Oximas

Las oximas [3] se obtienen por reacción de aldehídos o cetonas [1] e hidroxilamina [2] en un medio débilmente ácido. El mecanismo es análogo al de formación de iminas.



Las oximas de aldehídos y cetona asimétricas presentan isomería Z/E dependiendo de la posición del hidroxilo.



Las iminas e hidrazonas (que comentaremos a continuación) también presentan esta característica.

George A. Olah (1927 -)



Origen: Químico estadounidense.

Lugar de nacimiento: Budapest

Formación: Se doctoró en la Universidad de Budapest en 1949

Docencia: Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

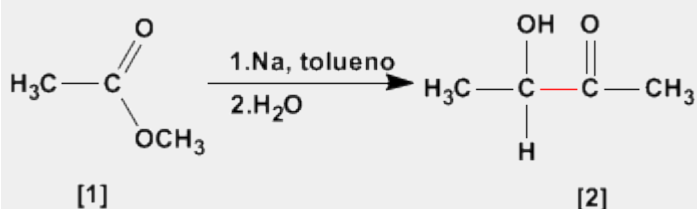
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Premio Nobel: En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

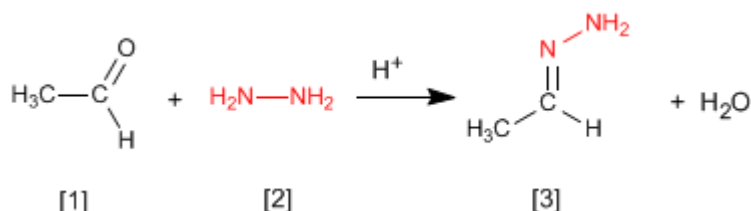
Aciloinica (Condensación)

La condensación aciloinica transforma ésteres [1] en alfa-hidroxicetonas [2]. Esta reacción se realiza con sodio metal en disolvente inerte.

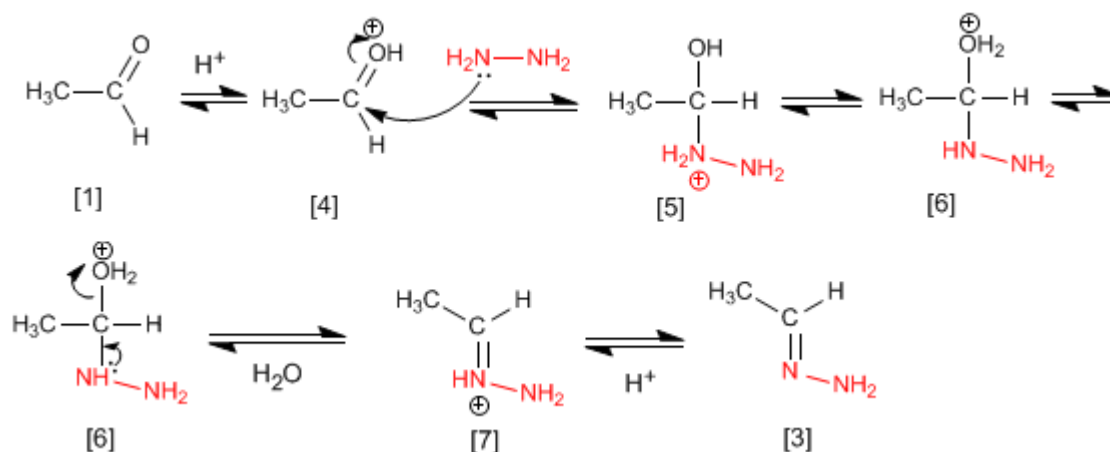


Formación de Hidrazonas

Las hidrazonas **[3]** se obtienen por reacción de aldehídos o cetonas **[1]** con hidrazina **[2]**. Igual que en el caso de las iminas y oximas requiere pH=4.



Aunque el mecanismo es análogo al de formación de iminas, comentaremos de nuevo los pasos.



El etanal **[1]** se protona formando su ácido conjugado **[4]**. La importante polaridad del carbono carbonilo de **[4]** favorece el ataque de la hidrazina **[2]** para formando el intermedio **[5]**. El compuesto **[5]** intercambia un protón entre el nitrógeno y el oxígeno, transformando el grupo hidroxilo en agua (buen grupo saliente). El intermedio **[6]** pierde una molécula de agua transformándose en **[7]**, cuya desprotonación da la hidrazona final **[3]**.

Kurt Alder (1902 - 1958)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

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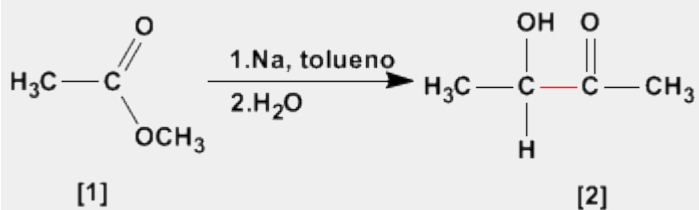
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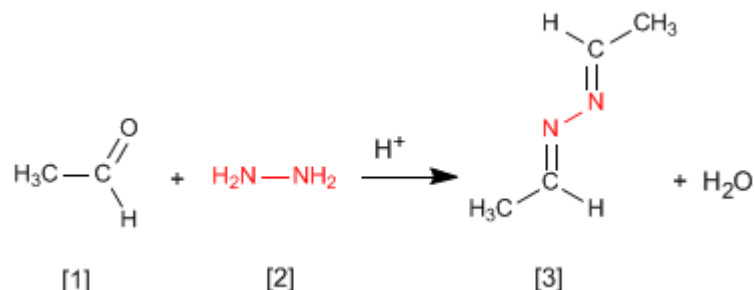
Aciloínica (Condensación)

La condensación aciloínica transforma esteres [1] en alfa-hidroxicetonas [2]. Esta reacción se realiza con sodio metal en disolvente inerte.



Formación de Azinas

La hidrazina [2] reacciona con dos moléculas de aldehído [1] para formar azinas [3].



El mecanismo es análogo al de formación de iminas, oximas e hidrazonas.

George A. Olah (1927 -)



Origen: Químico estadounidense.

Lugar de nacimiento: Budapest

Formación: Se doctoró en la Universidad de Budapest en 1949

Docencia: Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la

Universidad de Cleveland.

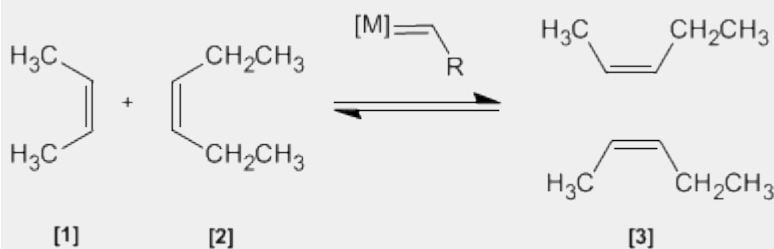
Industria: Trabajó en los laboratorios de la Dow Chemical de Ontario

Investigación: Olah consiguió preparar carbocationes estables utilizando componentes extremadamente ácidos.

Premio Nobel: En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

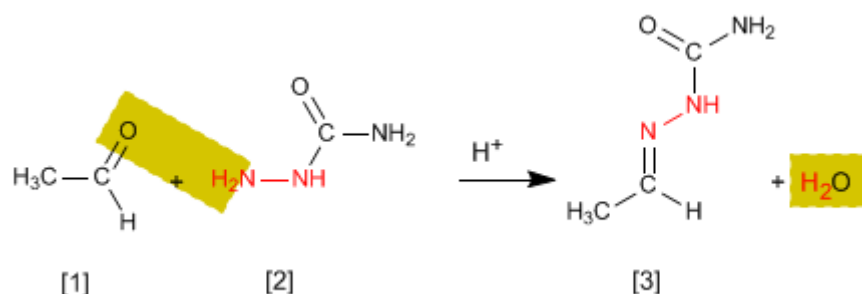
Metátesis de Alquenos

En esta reacción dos alquenos [1] y [2] son tratados con un metal de transición que actúa como catalizador, dando una mezcla de alquenos [3] (incluyendo isómeros Z/E). Este producto se obtiene por intercambio de grupos alquilideno.



Formación de Semicarbazonas

Las semicarbazonas [3] se obtienen por reacción de aldehídos o cetonas [1] con semicarbazida [2]. Veamos un ejemplo:



El mecanismo es análogo al de formación de iminas, oximas e hidrazonas.

Charles Friedel (1832 - 1899)



Origen: Químico frances..

Lugar de nacimiento: Estrasburgo.

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

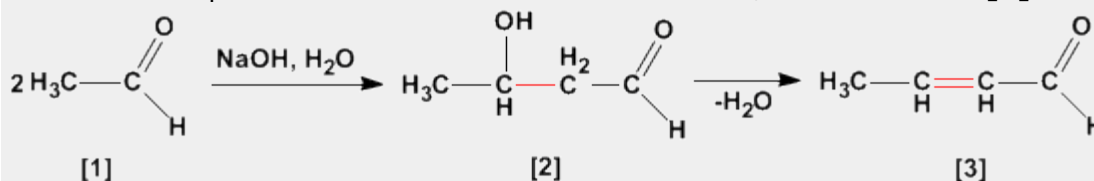
Docencia: Profesor en la Universidad de la Sorbona.

Investigación: Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

Premio Nobel:

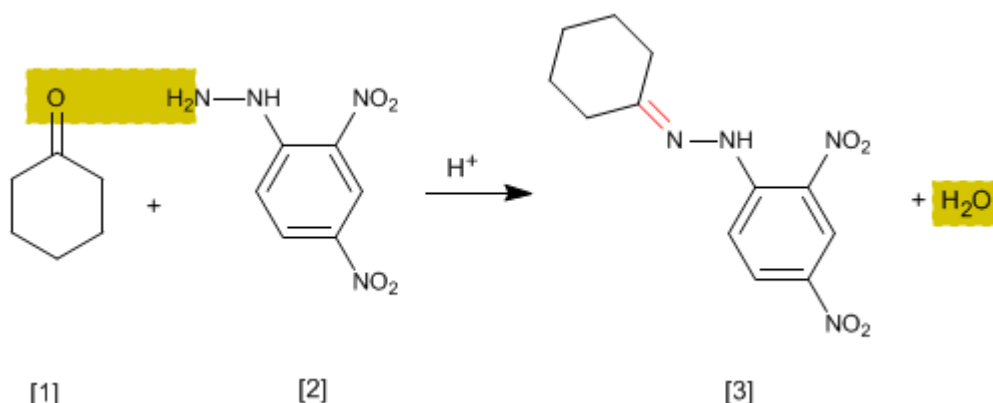
Aldólica (Condensación)

La condensación aldólica es una reacción de aldehídos o cetonas [1] que forma 3-hidroxicarbonilos (aldoles) [2]. El 3-hidroxiacetaldehído [2] bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado [3].



Ensayo de la 2,4-Dinitrofenilhidrazina

Se trata de un ensayo analítico específico de aldehídos y cetonas. Los carbonilos **[1]** reaccionan con 2,4-Dinitrofenilhidrazina **[2]** formando fenilhidrazonas **[3]** que precipitan de color amarillo. La aparición de precipitado es un indicador de la presencia de carbonilos en el medio.



El mecanismo de la reacción es análogo al de formación de iminas.

Kurt Alder (1902 - 1958)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

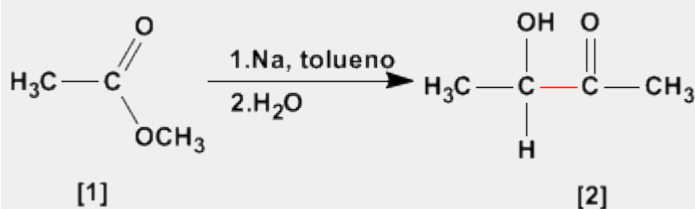
Docencia: Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

Investigación: Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos. Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

Premio Nobel: En 1950 recibió el Premio Nobel junto a Diels

Aciloinica (Condensación)

La condensación aciloinica transforma esteres **[1]** en alfa-hidroxicetonas **[2]**. Esta reacción se realiza con sodio metal en disolvente inerte.



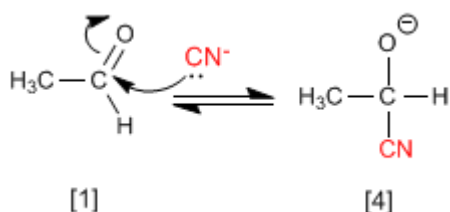
Formación de Cianhidrinas

Las cianhidrinas **[3]** se forman por reacción de aldehídos o cetonas **[1]** con ácido cianhídrico **[2]** y son compuestos que contienen un grupo ciano y un hidroxilo sobre el mismo carbono.

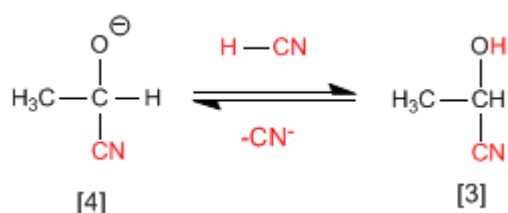


El mecanismo de la reacción transcurre en dos etapas:

Etapas 1. Los iones cianuro actúan como nucleófilos atacando al carbono carbonilo. El ácido cianhídrico es demasiado débil para generar cantidades importantes de cianuro, por ello, se añade cianuro de sodio o potasio al medio, garantizando la cantidad suficiente de cianuro para que la reacción transcurra en buen rendimiento.



Etapas 2. En este paso el ión alcóxido **[4]** se protona arrancando hidrógenos al ácido cianhídrico. En esta etapa se regeneran los iones cianuro.



Kurt Alder (1902 - 1958)



Origen: Químico alemán.

Lugar de nacimiento: Königshütte (hoy Chorzów, Polonia).

Formación: estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

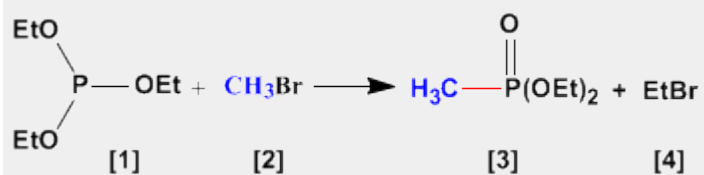
Docencia: Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

Investigación: Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos. Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

Premio Nobel: En 1950 recibió el Premio Nobel junto a Diels

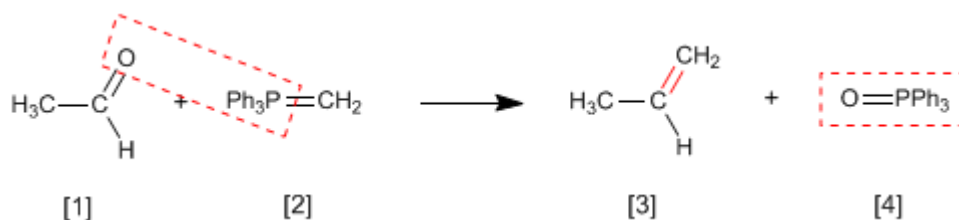
Arbuzov (Reacción)

La reacción de Arbuzov se emplea en la síntesis de fosfonatos **[3]** a partir de fosfitos **[1]**. Los fosfonatos obtenidos en la síntesis de Arbuzov se emplean como materiales de partida en la síntesis de Horner-Wittig.



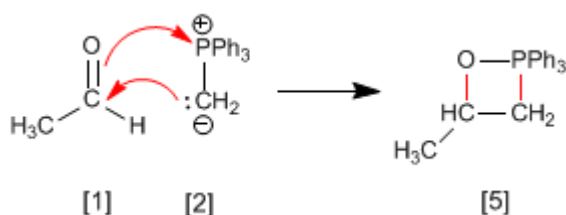
Reacción de Wittig

La reacción de Wittig emplea iluros de fósforo [2] para transformar aldehídos y cetonas [1] en alquenos [3]. Como subproducto se obtiene el óxido de trifenilfosfina [4].

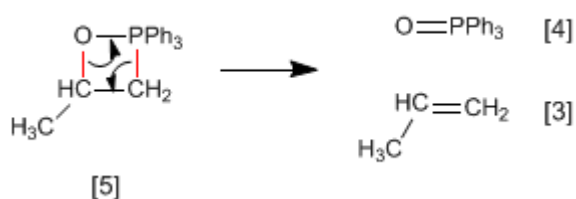


En el mecanismo de la reacción el iluro y el carbonilo se combinan para formar un oxafosfetano que rompe dejando libre el alqueno final.

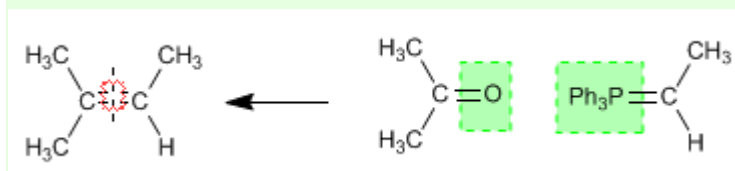
Etapas 1. El etanal y el iluro se combinan formando el fosfetano.



Etapas 2. El fosfetano rompe formando el alqueno y óxido de trifenilfosfina.



Ejemplo - Obtener mediante Wittig el 2-Metilbut-2-eno



Se rompe el alqueno por el doble enlace y a cada carbono se le agrega el grupo encerrado en verde.

Los **iluros de fósforo** se preparan mediante reacción de haloalcanos y trifenilfosfina, seguido de desprotonación del carbono con base fuerte (organometálicos de litio).



Charles Friedel (1832 - 1899)



Origen: Químico frances..

Lugar de nacimiento: Estrasburgo.

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

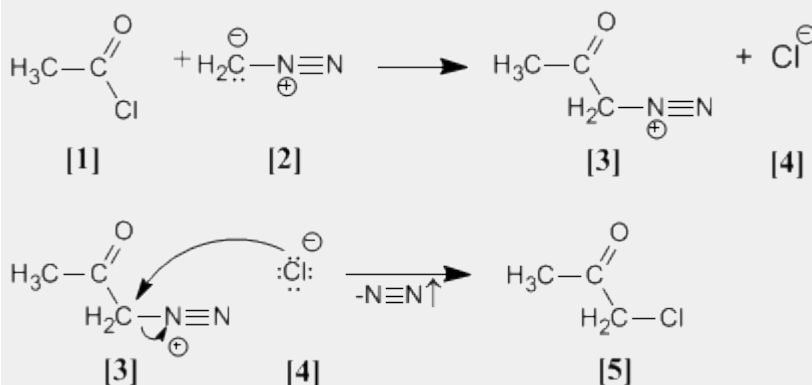
Docencia: Profesor en la Universidad de la Sorbona.

Investigación: Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

Premio Nobel:

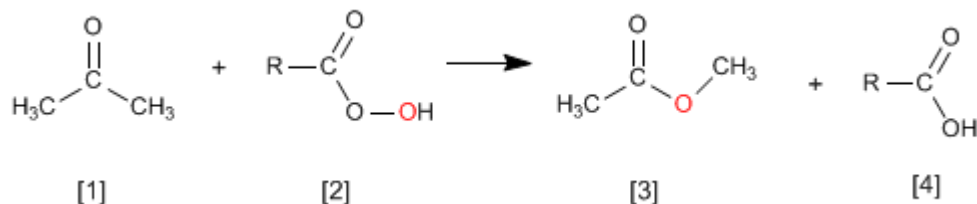
Arndt Eistert (Síntesis)

Cloruro de acetilo **[1]** se trata con diazometano **[2]** rindiendo la sal de diazonio **[3]**. El cloruro **[4]** producido reacciona con la sal de diazonio para dar la α-clorocetona **[5]**.

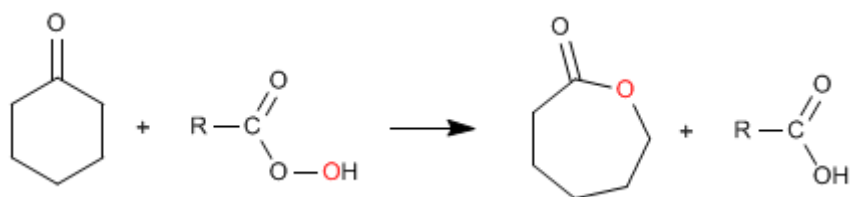


Oxidación de Baeyer Villiger

La reacción de cetonas **[1]** con perácidos **[2]** produce ésteres **[3]**. El oxígeno del perácido se inserta entre el carbono carbonilo y el carbono alfa de la cetona. Esta reacción fue descrita por Adolf von Baeyer y Victor Villiger in 1899.

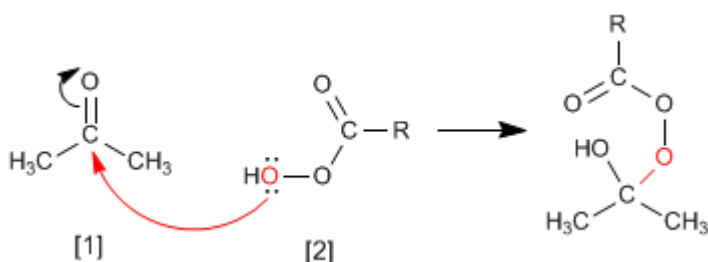


A partir de cetonas cíclicas se obtienen ésteres cíclicos (lactonas)

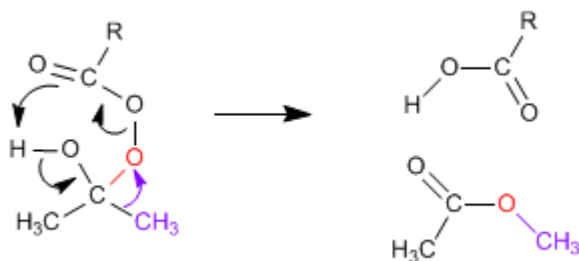


El mecanismo de Baeyer Villiger comienza con el ataque nucleófilo del perácido sobre el carbonilo, seguido de la migración del sustituyente desde el grupo carbonilo al oxígeno del perácido.

Etapas 1. Adición del perácido al carbonilo

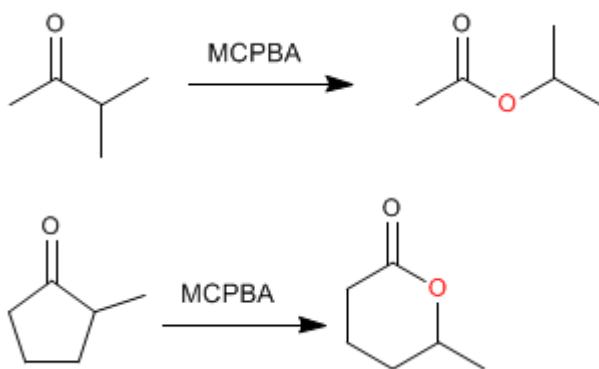


Etapas 2. Migración del sustituyente desde carbono carbonilo hacia el oxígeno (rojo)



Cuando la cetona tiene dos sustituyentes diferentes migra mejor el más sustituido. Existe un orden de migración que nos ayuda a decidir que sustituyente pasa a unirse al oxígeno del perácido.

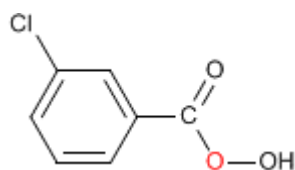
Orden de migración: H > carbono terciario > ciclohexilo > carbono secundario » fenilo > carbono primario > metilo



Como puede observarse en el orden de migración, el grupo que mejor migra, por su pequeño tamaño, es el hidrógeno, por ello, al tratar aldehídos con perácidos se produce la migración del hidrógeno formándose ácidos carboxílicos.



El **MCPBA** (Ácido meta-cloroperoxibenzoico) es un perácido ampliamente utilizado en la epoxidación de alquenos y también en Baeyer-Villiger. La fórmula del MCPBA se muestra a continuación.



Charles Friedel (1832 - 1899)



Origen: Químico frances..

Lugar de nacimiento: Estrasburgo.

Formación: estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

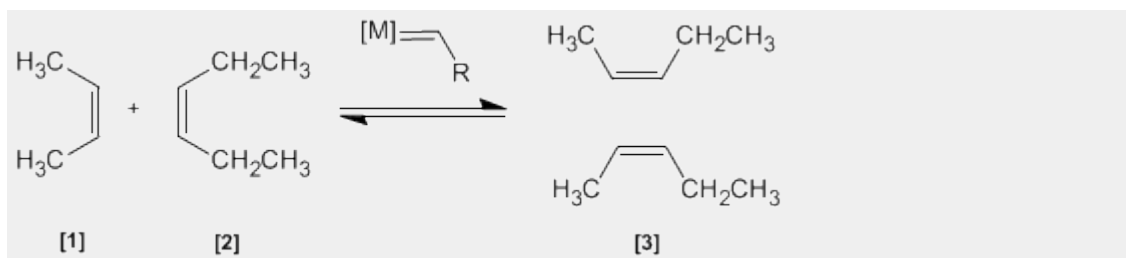
Docencia: Profesor en la Universidad de la Sorbona.

Investigación: Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

Premio Nobel:

Metátesis de Alquenos

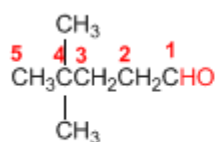
En esta reacción dos alquenos **[1]** y **[2]** son tratados con un metal de transición que actúa como catalizador, dando una mezcla de alquenos **[3]** (incluyendo isómeros Z/E). Este productos se obtiene por intercambio de grupos alquilideno.



Nomenclatura de Aldehídos y Cetonas - Reglas IUPAC

Regla 1. Los aldehídos se nombran reemplazando la terminación **-ano** del alcano correspondiente por **-al**. No es necesario especificar la posición del grupo aldehído, puesto que ocupa el extremo de la cadena (localizador 1).

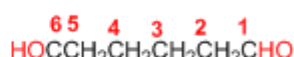
Cuando la cadena contiene dos funciones aldehído se emplea el sufijo **-dial**.



4,4-Dimetilpentanal

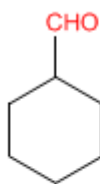


Hex-4-enal

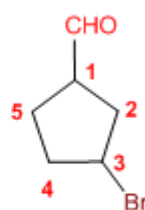


Hexanodial

Regla 2. El grupo **-CHO** se denomina **-carbaldehído**. Este tipo de nomenclatura es muy útil cuando el grupo aldehído va unido a un ciclo. La numeración del ciclo se realiza dando localizador 1 al carbono del ciclo que contiene el grupo aldehído.

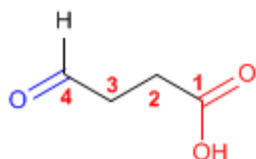


Ciclohexanocarbaldehído

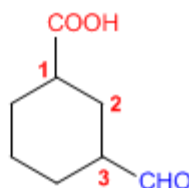


3-Bromociclopentanocarbaldehído

Regla 3. Cuando en la molécula existe un grupo prioritario al aldehído, este pasa a ser un sustituyente que se nombra como oxo- o formil-.



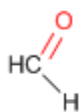
Ácido 4-oxobutanoico



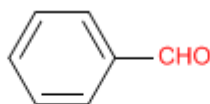
Ácido 3-formilciclohexanocarboxílico

Tanto **-carbaldehído** como **formil-** son nomenclaturas que incluyen el carbono del grupo carbonilo. **-carbaldehído** se emplea cuando el aldehído es grupo funcional, mientras que **formil-** se usa cuando actúa de sustituyente.

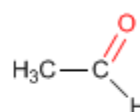
Regla 4. Algunos nombres comunes de aldehídos aceptados por la IUPAC son:



Formaldehído
(Metanal)

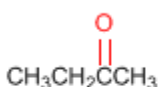


Benzaldehído
(Benceno**carbaldehído**)

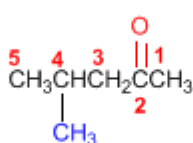


Acetaldehído
(Etanal)

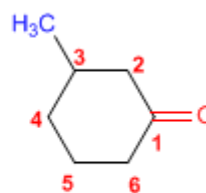
Regla 5. Las cetonas se nombran sustituyendo la terminación **-ano** del alcano con igual longitud de cadena por **-ona**. Se toma como cadena principal la de mayor longitud que contiene el grupo carbonilo y se numera para que éste tome el localizador más bajo.



Butan**ona**

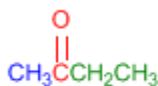


4-Metil-2-pentan**ona**

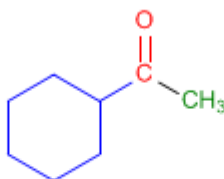


3-Metilciclohexan**ona**

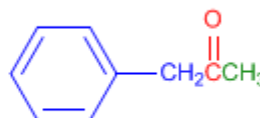
Regla 6. Existe un segundo tipo de nomenclatura para las cetonas, que consiste en nombrar las cadenas como sustituyentes, ordenándolas alfabéticamente y terminando el nombre con la palabra cetona.



Etil metil **cetona**

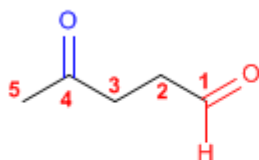


Ciclohexil metil **cetona**

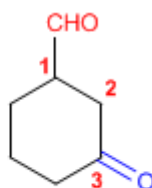


Fenil metil **cetona**

Regla 7. Cuando la cetona no es el grupo funcional de la molécula pasa a llamarse **OXO-**.



4-Oxopentan**al**

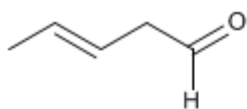


3-Oxociclohexano**carbaldehído**

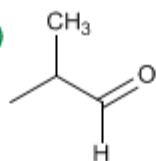
Nomenclatura de Aldehídos y Cetonas - Problema 9.1

Nombra los siguientes aldehídos y cetonas:

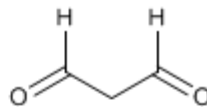
a)



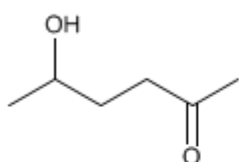
b)



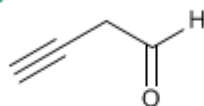
c)



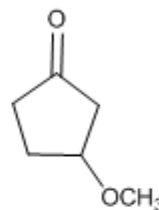
d)



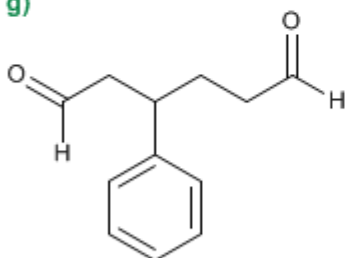
e)



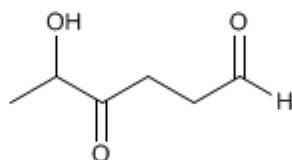
f)



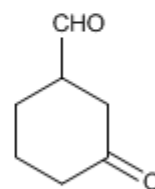
g)



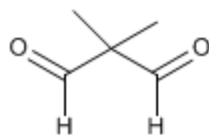
h)



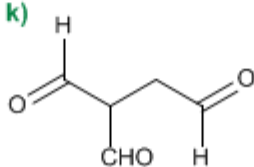
i)



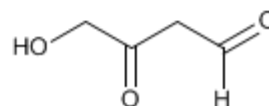
j)



k)

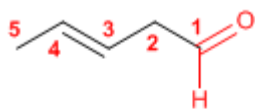


l)

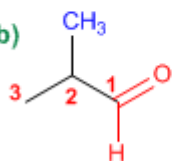


Solución

a)



b)



1. Cadena principal: 5 carbonos (pentano)

2. Numeración: comienza en el aldehído (grupo funcional)

Grupo funcional: aldehído

3. Nombre: Pent-3-enal

1. Cadena principal: 3 carbonos (propano)

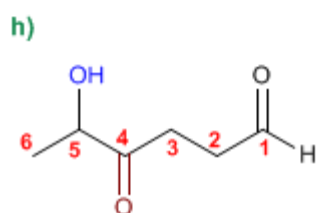
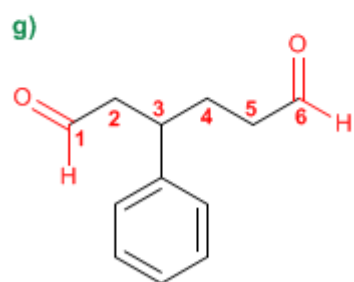
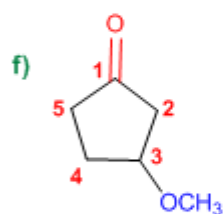
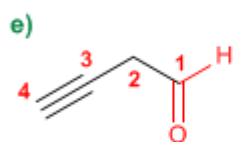
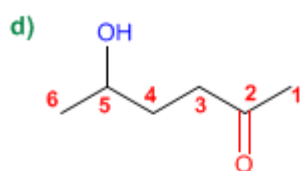
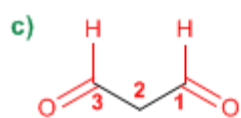
2. Numeración: localizador más bajo al aldehído.

3. Grupo funcional: aldehído

4. Sustituyentes: metilo en 2.

5. Nombre: 2-Metilpropanal

Los aldehídos y cetonas son prioritarios sobre alquenos y alquinos, y se numeran otorgándoles el localizador más bajo



1. Cadena principal: 3 carbonos (propano)
2. Grupo funcional: aldehído (dialdehído)
3. Nombre: Propanodial

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: cetona
3. Numeración: asignar el menor localizador a la cetona
4. Sustituyentes: hidroxí en 5.
5. Nombre: 5-Hidroxihexan-2-ona

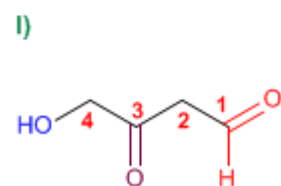
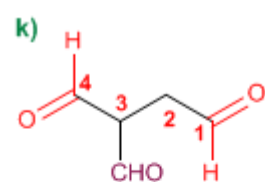
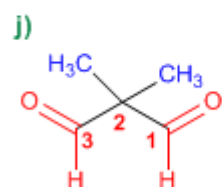
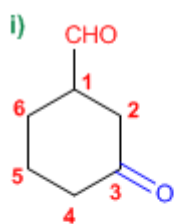
1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Nombre: But-3-inal

1. Cadena principal: ciclo de 5 miembros (ciclopentano)
2. Grupo funcional: cetona
3. Numeración: comienza en la cetona y prosigue hacia el sustituyente
4. Sustituyentes: metoxi en 3.
5. Nombre: 3-Metoxiciclopentanona

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: aldehído (dialdehído)
3. Numeración: comienza en el extremo que otorga al fenilo el localizador más bajo.
4. Sustituyentes: fenilo en 3.
5. Nombre: 3-Fenilhexanodial

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Sustituyentes: hidroxí en 5 y oxo en 4.
5. Nombre: 5-Hidroxí-4-oxohexanal

Los aldehídos son prioritarios sobre las cetonas que pasan a nombrarse como sustituyentes (oxo-)



1. Cadena principal: ciclo de 6 miembros (ciclohexano)
2. Grupo funcional: aldehído (-carbaldehído)
3. Numeración: menor localizador al grupo -CHO (este no se numera)
4. Sustituyentes: cetona (oxo-) en 3
5. Nombre: 3-Oxociclohexanocarbaldehído

1. Cadena principal: 3 carbonos (propano)
2. Grupo funcional: aldehído (dialdehído)
3. Sustituyentes: metilos en 2,2.
4. Nombre: 2,2-Dimetilpropanodial

1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Sustituyentes: formil en 3
4. Nombre: 3-Formilbutanodial

1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Sustituyentes: hidroxil en 4 y oxo en 3.
5. Nombre: 4-Hidroxil-3-oxobutanal

Nomenclatura de Aldehídos y Cetonas - Problema 9.2

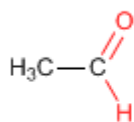
PRINT EMAIL

Dibuja la estructura de los siguientes aldehídos y cetonas:

- | | |
|---|----------------------------------|
| a) Etanal (acetaldehído) | g) 2,5-Dioxooctanodial |
| b) 3-Metilbutanal | h) 1,3-Ciclohexanodiona |
| c) Benzaldehído | i) 3-Metil-3-pental |
| d) 4-Hidroxiciclohexanocarbaldehído | j) 3-Oxobutanal |
| e) 3-Hidroxi-4-metil-5-oxociclohexanocarbaldehído | k) 3-Hidroxiciclopentanona |
| f) 2-Metil-2,5-octanodiona | l) 4-Etoxi-5-fenil-3-oxoheptanal |

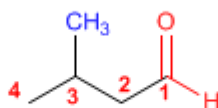
Solución

a)



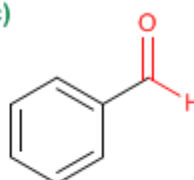
Etanal (acetaldehído)

b)

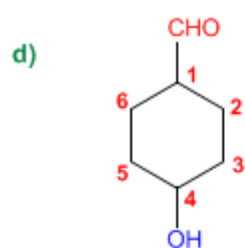


3-Metilbutanal

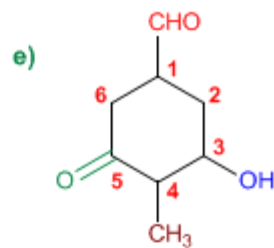
c)



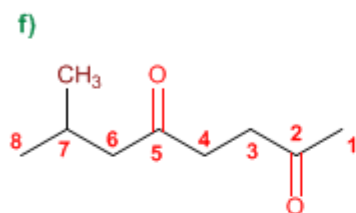
Benzaldehído



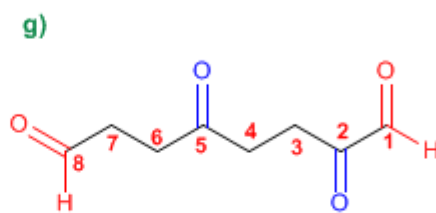
4-Hidroxiciclohexanocarbaldehído



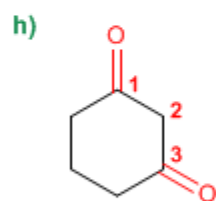
3-Hidroxi-4-metil-5-oxociclohexanocarbaldehído



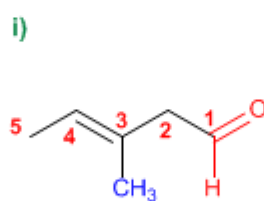
7-Metil-2,5-octanodiona



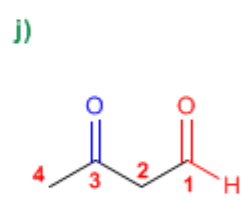
2,5-Dioxooctanal



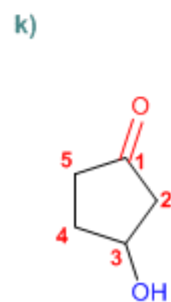
1,3-Ciclohexanodiona



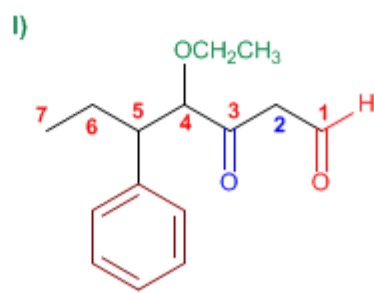
3-Metil-3-pentenal



3-Oxobutanal



3-Hidroxiciclopentanona

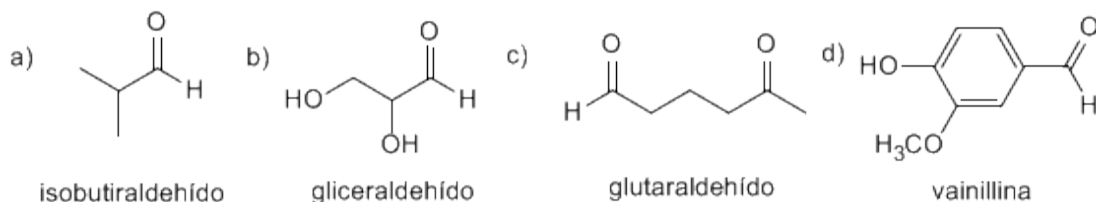


4-Etoxi-5-fenil-3-oxoheptanal

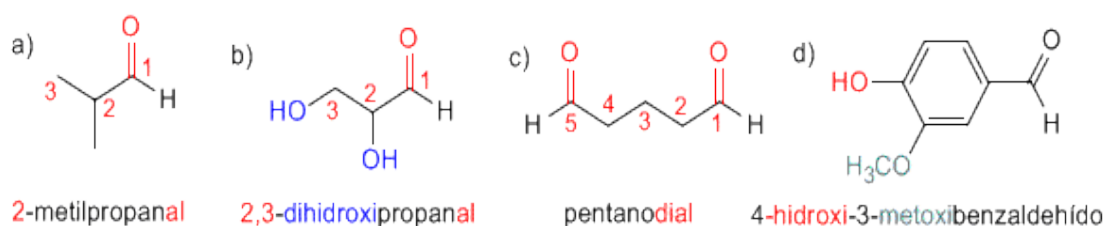
PROBLEMAS RESUELTOS DE ALDEHÍDOS Y CETONAS

Aldehídos y Cetonas: Problema 1

1) A continuación se dan nombres comunes y las fórmulas estructurales de algunos compuestos carbonílicos. Indique el nombre correspondiente según la IUPAC.



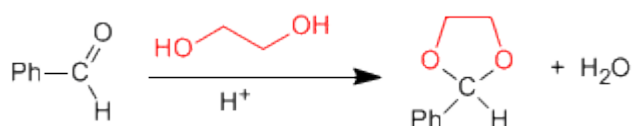
Solución



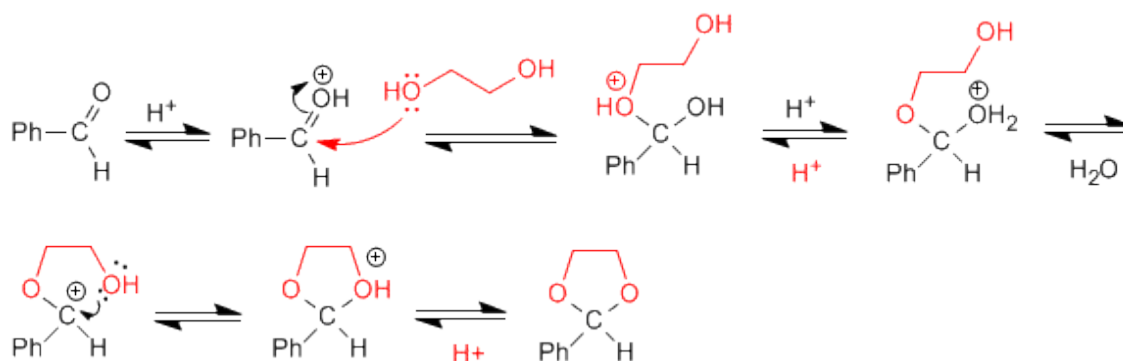
Aldehídos y cetonas: Problema 2

Dibuje la estructura del acetal que se forma cuando el benzaldehído se calienta con 1,2-etanodiol en medio ácido. Escriba un mecanismo detallado que justifique su formación. Describa paso a paso la hidrólisis de este acetal en medio ácido acuoso.

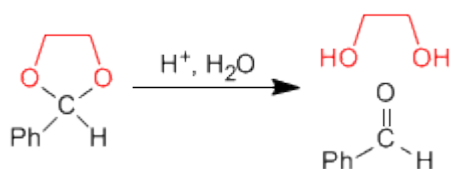
SOLUCIÓN



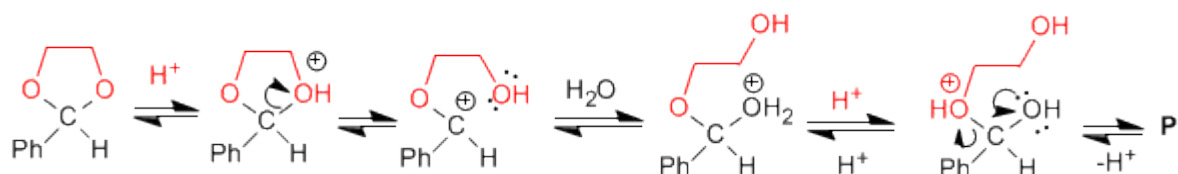
Mecanismo de formación del acetal:



La hidrólisis del acetal en medio ácido acuoso sigue es etapas inversas a la síntesis.



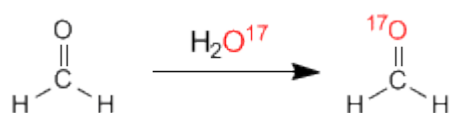
Mecanismo de hidrólisis del acetal cíclico.



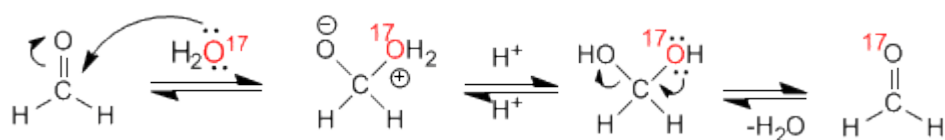
Aldehídos y Cetonas: Problema 3

Cuando se disuelve formaldehído en agua marcada con ^{17}O , se observa que después de unas horas tanto el hidrato del formaldehído como el formaldehído han incorporado el isótopo ^{17}O . Sugiera una explicación razonable de este hecho.

SOLUCION



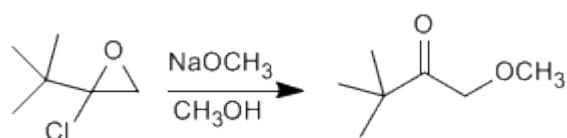
Mecanismo:



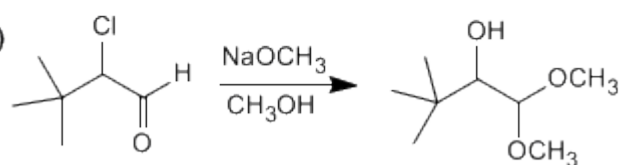
Aldehídos y Cetonas: Problema 4

Sugiera un mecanismo razonable para una de las siguientes reacciones:

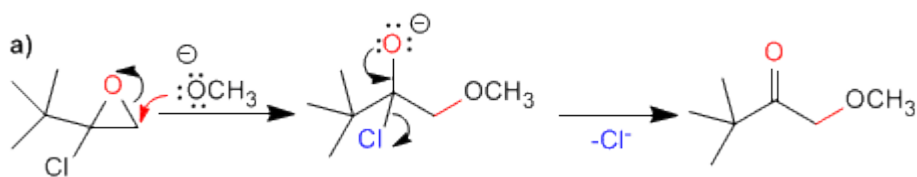
a)



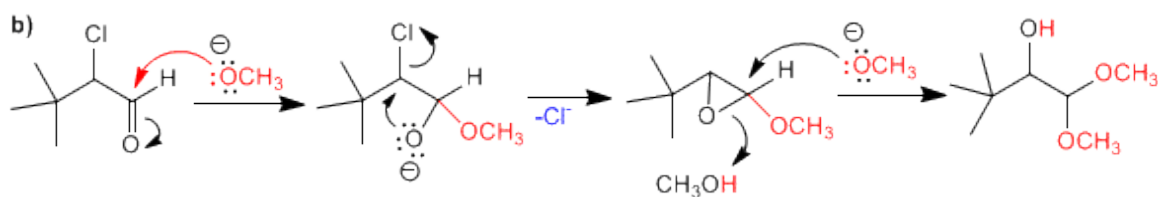
b)



SOLUCION



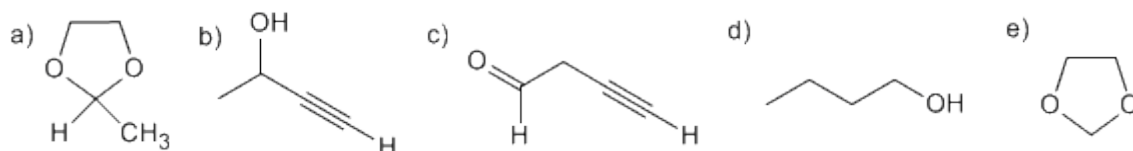
La primera etapa consiste en la apertura del oxaciclopropano sobre el carbono menos sustituido. En la segunda etapa, la cesión del par del oxígeno elimina el cloro, formándose un carbonilo.



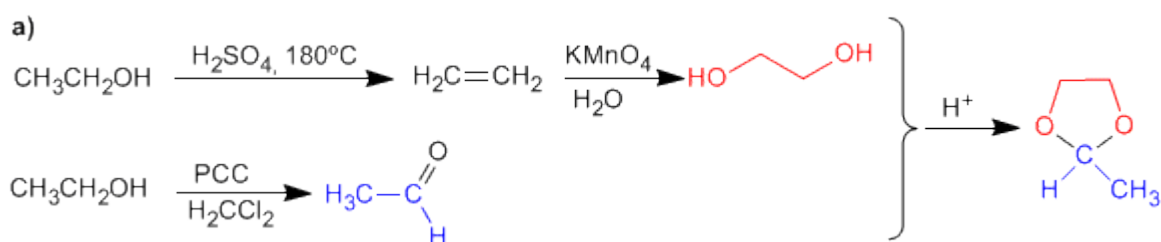
En el primer paso hay dos posibles posiciones de ataque; el carbono carbonilo y el carbono del cloro. Como el producto final no tiene metóxido en el carbono del cloro, atacamos al carbonilo. En la segunda etapa se produce una sustitución nucleófila intramolecular. Para terminar el metóxido abre el epóxido.

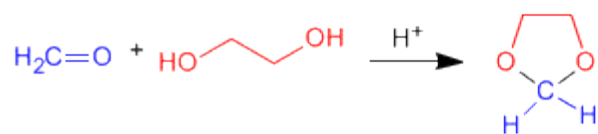
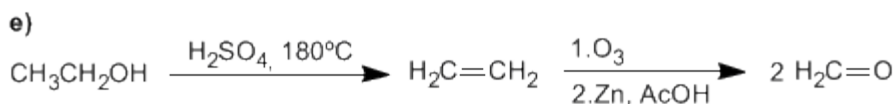
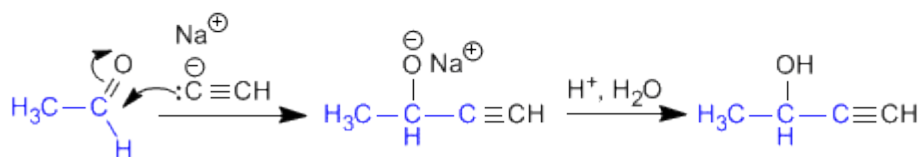
Aldehídos y Cetonas: Problema 5

Usando etanol como fuente de todos los átomos de carbono y los reactivos que necesite, describa una síntesis eficiente de cada una de las sustancias siguientes:

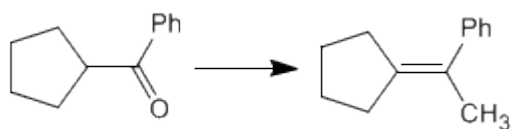


SOLUCIÓN





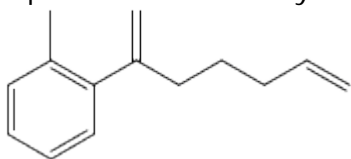
Utilizando los reactivos necesarios, indicar las etapas que permiten realizar la siguiente transformación:



[2] Isomerización en medio ácido, impulsada por la mayor estabilidad del alqueno interno.

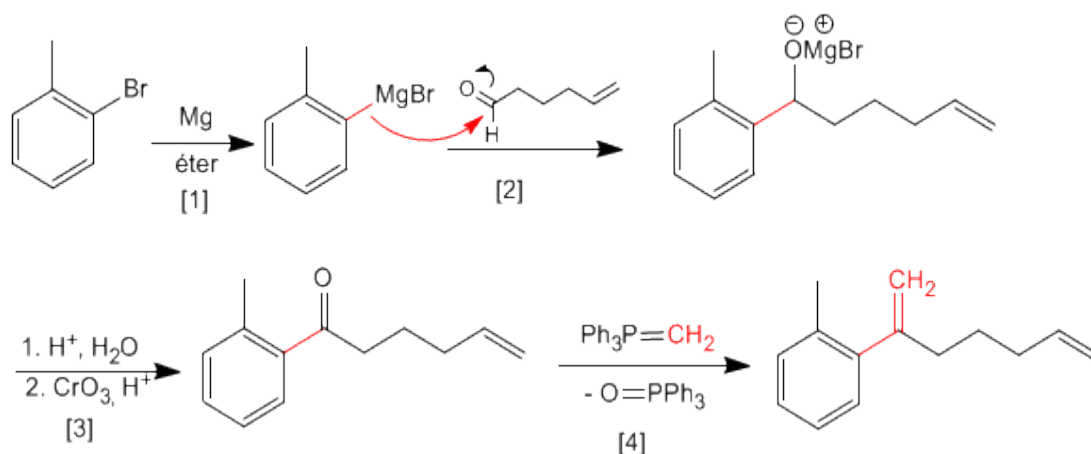
Aldehídos y Cetonas: Problema 7

A partir de 5-hexenal y o-bromotolueno obtener el siguiente producto.



Pueden ser necesarios reactivos orgánicos e inorgánicos adicionales.

SOLUCIÓN



[1] Formación del magnesiano

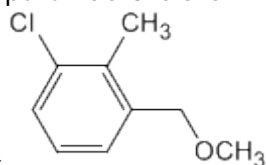
[2] Ataque nucleófilo del magnesiano al carbonilo.

[3] Hidrólisis y posterior oxidación del alcohol secundario.

[4] Reacción de Wittig entre la cetona y el trifenilmetilenfosforano.

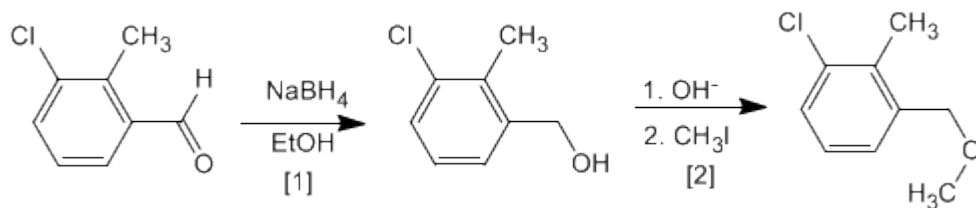
Aldehídos y Cetonas: Problema 8

Obtener a partir de 3-cloro-2-metilbenzaldehído y de los reactivos



necesarios
el compuesto siguiente:

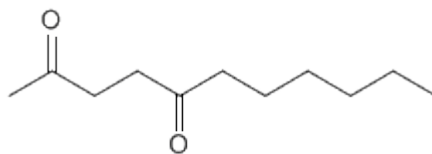
SOLUCIÓN



[1] Reducción del aldehído a alcohol

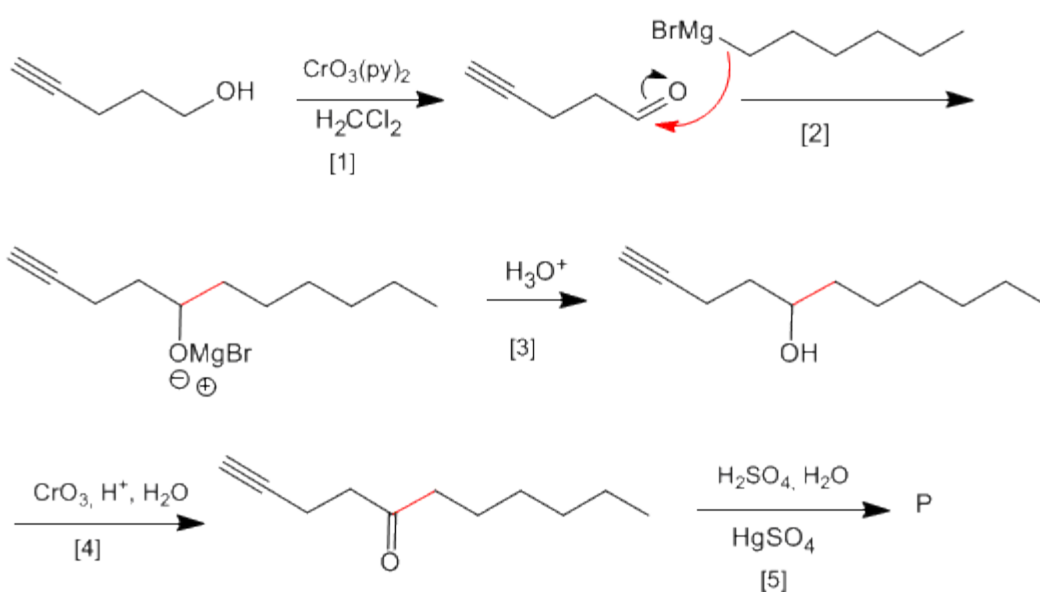
[2] Síntesis de Williamson de éteres.

Aldehídos y Cetonas: Problema 9



A partir de 4-pentin-1-ol obtener:

SOLUCIÓN

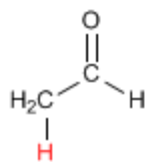


- [1] Oxidación del alcohol a aldehído
- [2] Formación del enlace carbono-carbono mediante organometálicos de magnesio
- [3] Protonación del alcohol
- [4] Oxidación del alcohol con Jones (Puedes utilizar también $\text{CrO}_3(\text{py})_2$)
- [5] Hidratación Markovnikov del alquino, para formar cetonas

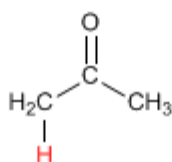
TEORÍA DE ENOLES Y ENOLATOS

Formación de Enolatos

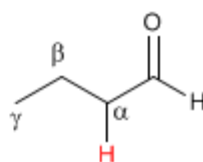
Los aldehídos y cetonas presentan hidrógenos ácidos en la posición vecina al grupo carbonilo, conocida como posición alfa. Estos hidrógenos presentan un pKa comprendido entre 18 y 21.



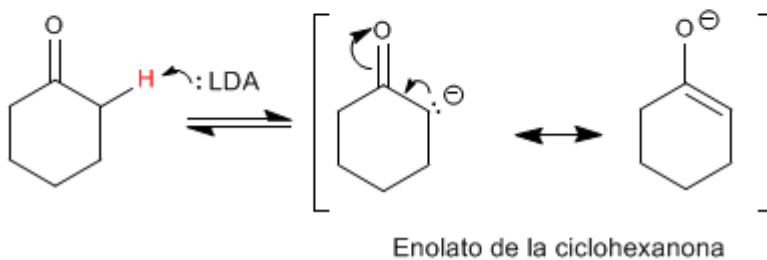
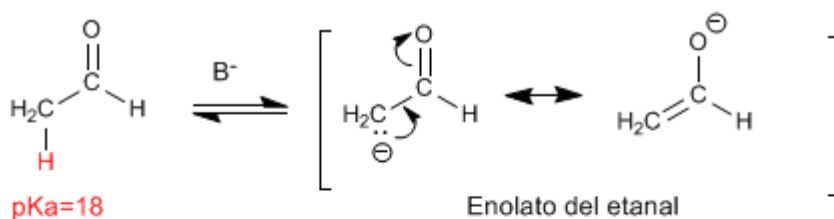
pKa=18



pKa=20-21



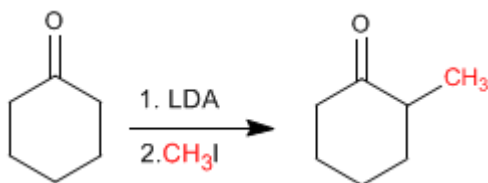
La acidez de los hidrógenos α es debida a la estabilización de la base conjugada (enolato) por resonancia.



Alquilación de Enolatos

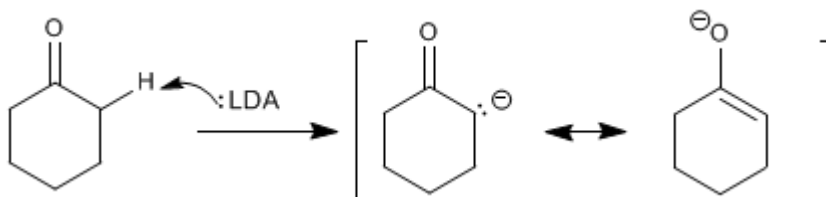
Los enolatos actúan como nucleófilos a través del carbono atacando a un gran número de electrófilos (haloalcanos, epóxidos, carbonilos, ésteres.....). En este punto nos fijaremos en la reacción entre enolatos y haloalcanos, que permite añadir cadenas carbonadas a la posición α de la cadena.

La Ciclohexanona se convierte en 2-Metilciclohexanona por tratamiento con LDA seguido de yoduro de metilo.

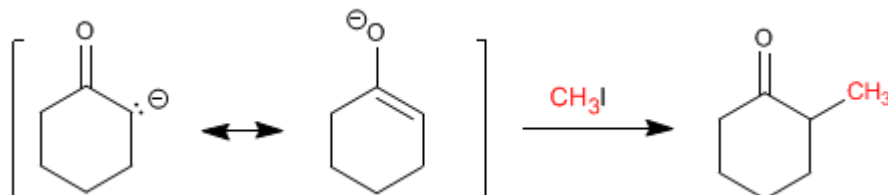


Etapas del mecanismo por el que se alquila la ciclohexanona:

Etapas 1. Formación del enolato

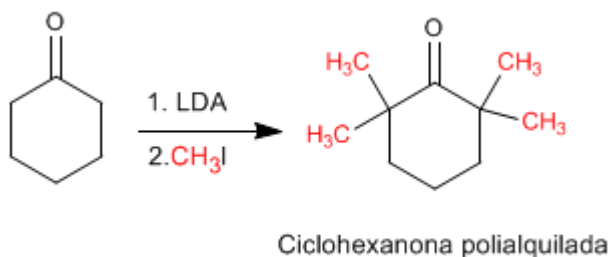


Etapas 2. Ataque nucleófilo del enolato sobre el haloalcano (Reacción de tipo $\text{S}_{\text{N}}2$)



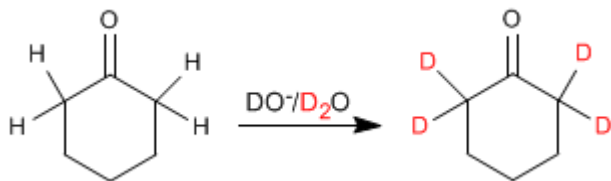
Las reacciones de alquilación tienen dos importantes problemas.

1. Competencia con la condensación aldólica. Los carbonilos en medio básico tienden a condensar para formar aldoles.
2. La reacción es difícil de controlar y tiende a polialquilar el carbonilo.



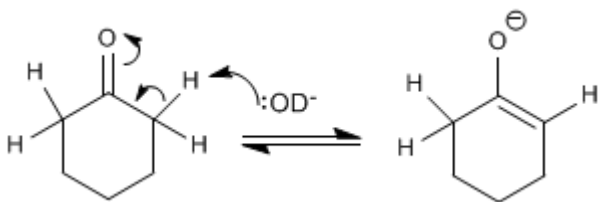
Intercambio hidrógeno - Deuterio

Los aldehídos y cetonas intercambian sus hidrógenos a por deuterios cuando se tratan con $\text{DO}^-/\text{D}_2\text{O}$ o con $\text{D}^+/\text{D}_2\text{O}$. En medios básicos la reacción transcurre a través de enolatos y en medios ácidos los intermediarios formados son enoles.

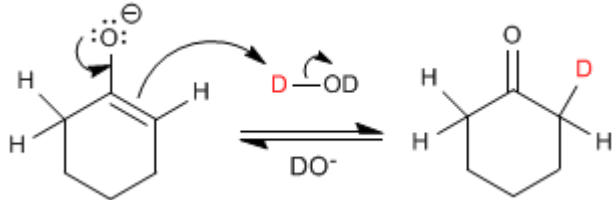


El mecanismo del intercambio hidrógeno-deuterio transcurre en los siguientes pasos:

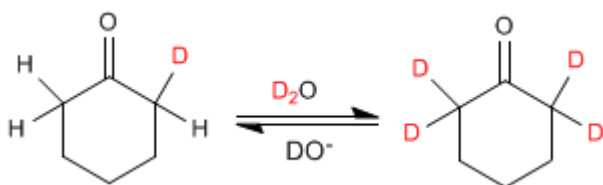
Etapla 1. Formación del enolato



Etapla 2. Transferencia del deuterio al enolato



Etapla 3. Sustitución del resto de hidrógenos



Halogenación de aldehídos y cetonas

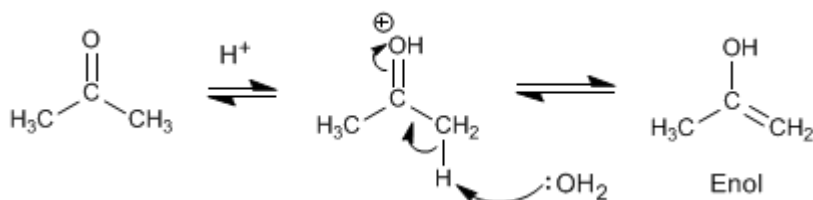
Los aldehídos y cetonas reaccionan con halógenos en medios ácidos o básicos produciéndose la sustitución de hidrógenos a por halógenos.

Halogenación de la propanona en medio ácido:

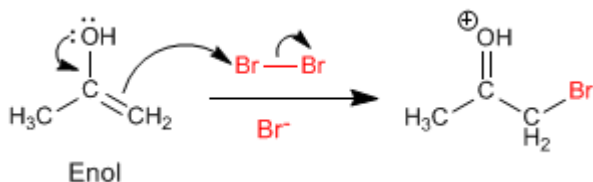


El mecanismo de halogenación en **medio ácido** tiene las siguientes etapas:

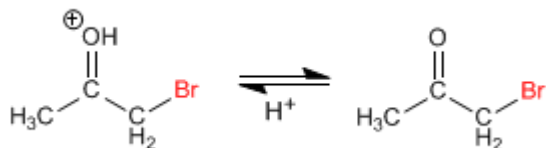
Etapas 1. Formación del enol



Etapas 2. Ataque nucleófilo del enol sobre el halógeno ayudado por la cesión del par del oxígeno.

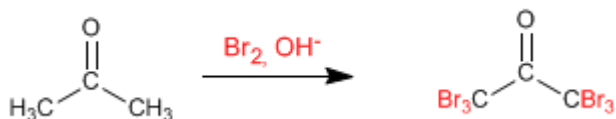


Etapas 3. Desprotonación



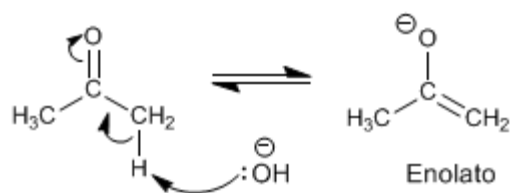
Trabajando con un equivalente de reactivo la halogenación para en una primera adición y no ocurren polihalogenaciones. El paso clave del mecanismo es la formación del enol y esta etapa requiere protonar el oxígeno del carbonilo. Una vez halogenada la posición α el oxígeno se vuelve menos básico, debido al efecto electronegativo del bromo, protonándose peor.

Halogenación de la propanona en **medio básico**:

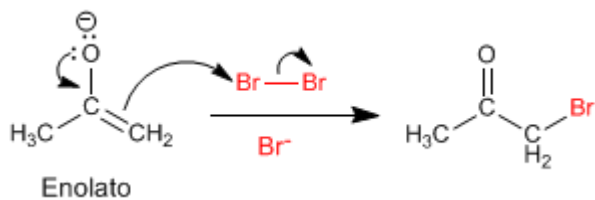


La halogenación en medio básico tiene el siguiente mecanismo:

Etapla 1. Formación del enolato



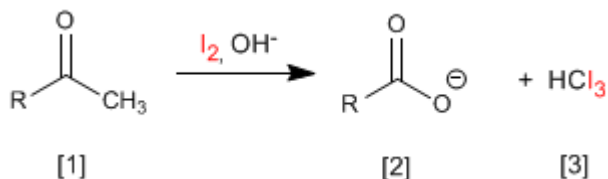
Etapla 2. Ataque nucleófilo del enolato sobre el halógeno ayudado por la cesión del para del oxígeno.



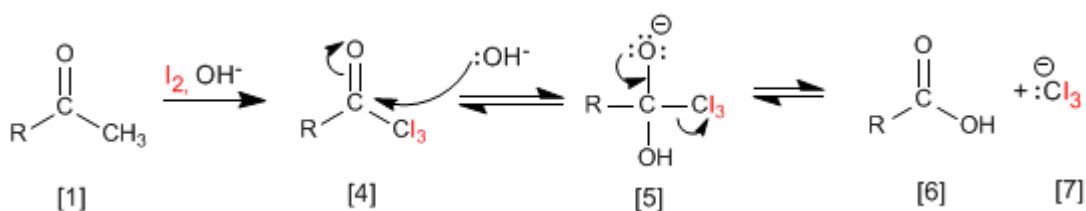
Este mecanismo se repite otras 5 veces sustituyendo todos los hidrógenos a por halógenos. En este caso la reacción no para puesto que el producto halogenado es más reactivo que la propanona de partida. La base arranca mejor los hidrógenos en el producto halogenado (son más ácidos), haciendo imposible parar la reacción.

Reacción del Haloformo (Yodoformo)

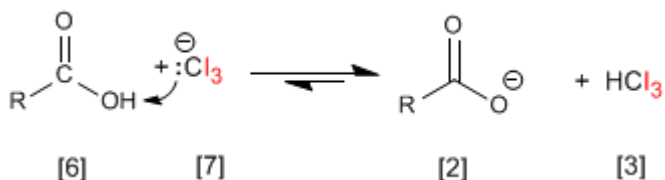
Las cetonas metílicas **[1]** reaccionan con halógenos en medios básicos generando carboxilatos **[2]** y haloformo **[3]**.



El mecanismo consiste en halogenar completamente el metilo, sustituyendo en una etapa posterior el grupo $-\text{CX}_3$ formado por $-\text{OH}$.



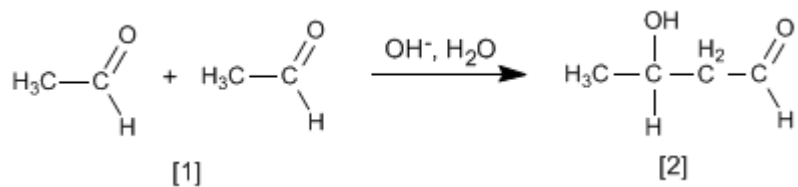
El grupo Cl_3^\ominus es muy básico y desprotona el ácido carboxílico formándose yodoformo y el carboxilato.



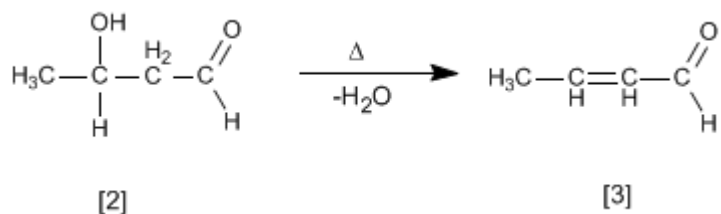
Esta reacción (con yodo) puede emplearse como ensayo analítico para identificar cetonas metílicas aprovechando que el yodoformo precipita de color amarillo.

Condensación Aldólica

Aldehídos y cetonas [1] condensan en medios básicos formando aldoles [2]. Esta reacción se denomina condensación aldólica.

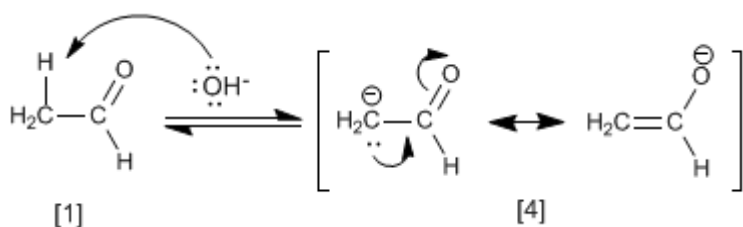


El aldol [2] formado deshidrata en el medio básico por calentamiento para formar un α,β -insaturado [3].



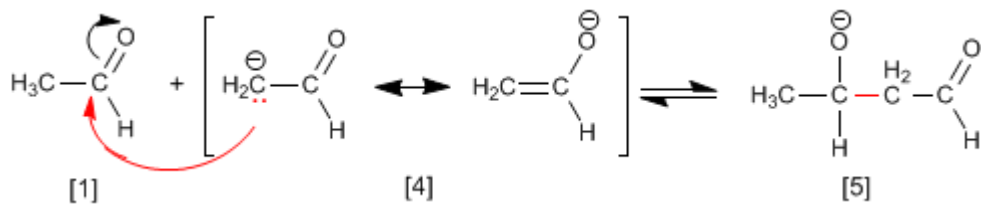
El mecanismo de la condensación aldólica transcurre con formación de un enolato, que ataca al carbonilo de otra molécula. En esta condensación se forma un enlace carbono-carbono entre el carbonilo de una molécula y el carbono α de la otra.

Etapas 1. Formación del enolato

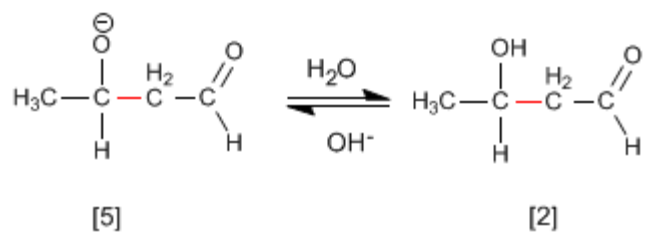


La base desprotona el carbono α del etanal [1] generando el enolato [4] estabilizado por resonancia.

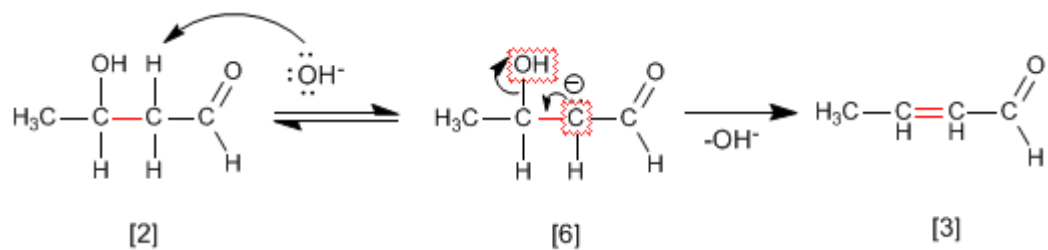
Etapas 2. Ataque nucleófilo del enolato sobre el carbonilo



Etapas 3. Protonación

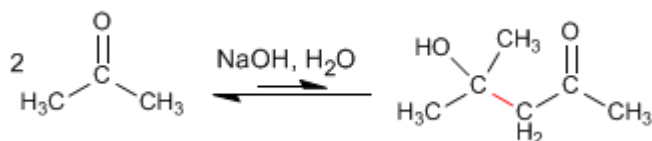


Etapas 4. Deshidratación del aldol

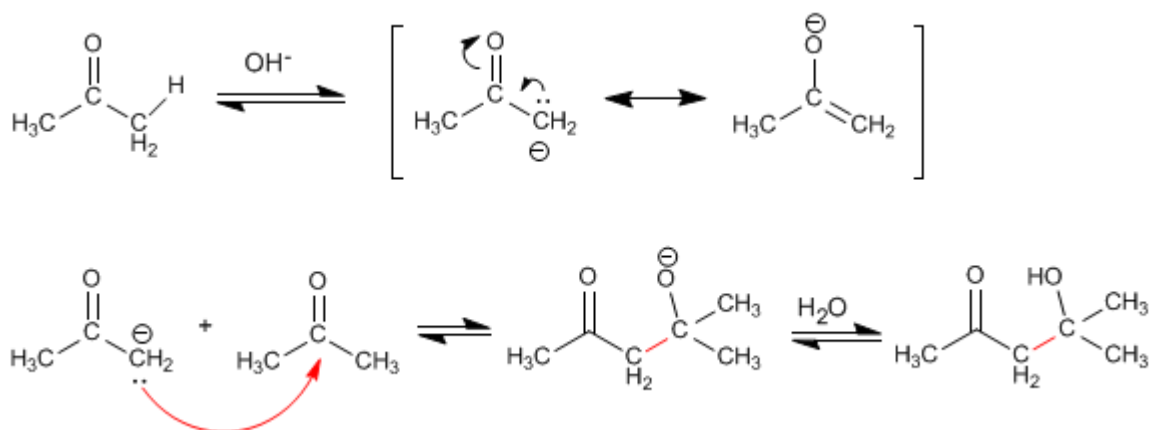


Condensación aldólica con cetonas

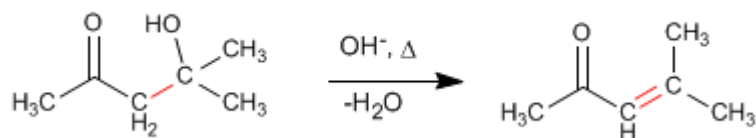
Las cetonas son menos reactivas que los aldehídos y dan un rendimiento muy bajo en la condensación aldólica. Así, dos moléculas de propanona condensan para formar el aldol correspondiente con un rendimiento del 2%. Se pueden conseguir porcentajes elevados del producto separándolo del medio de reacción según se va formando, o bien, calentando para deshidratarlo. De ambas formas los equilibrios de la aldólica se desplazan hacia el producto final.



Mecanismo de la reacción:



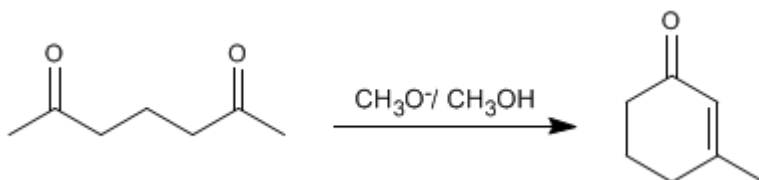
La deshidratación final permite el desplazamiento de los equilibrios. También se puede realizar una extracción del aldol del medio de reacción para favorecer la reacción.



Condensación aldólica intramolecular

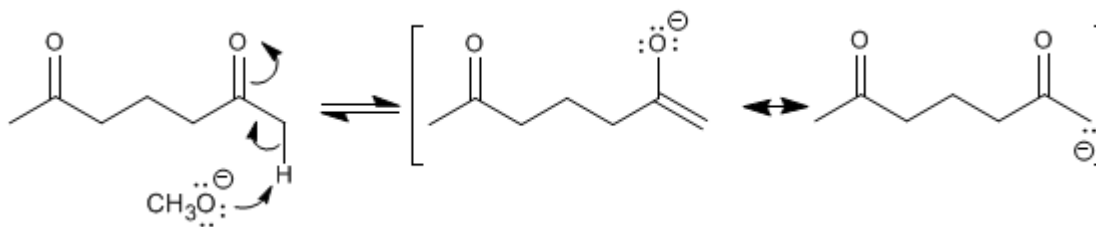
Los compuestos dicarbonílicos condensan mediante la aldólica intramolecular en medios básicos. En esta reacción se obtienen ciclos de cinco o seis miembros.

Así, la 2,6-heptanodiona condensa con metóxido en metanol para formar el 3-metilciclohex-2-enona.

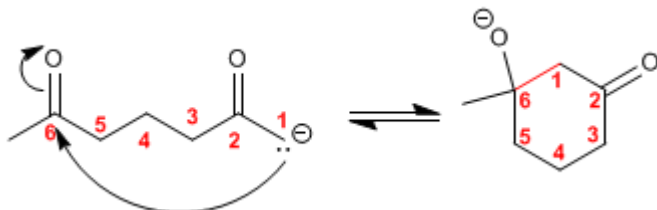


El mecanismo de la reacción transcurre a través de las siguientes etapas:

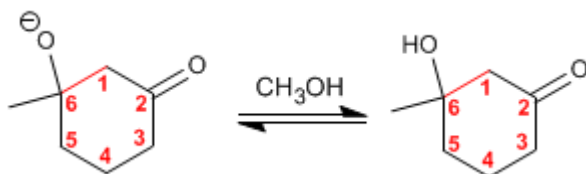
Etapas 1. Formación del enolato.



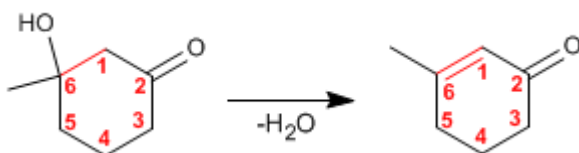
Etapas 2. Adición nucleófila intramolecular



Etapas 3. Protonación de la base del aldol



Etapas 4. Deshidratación del aldol

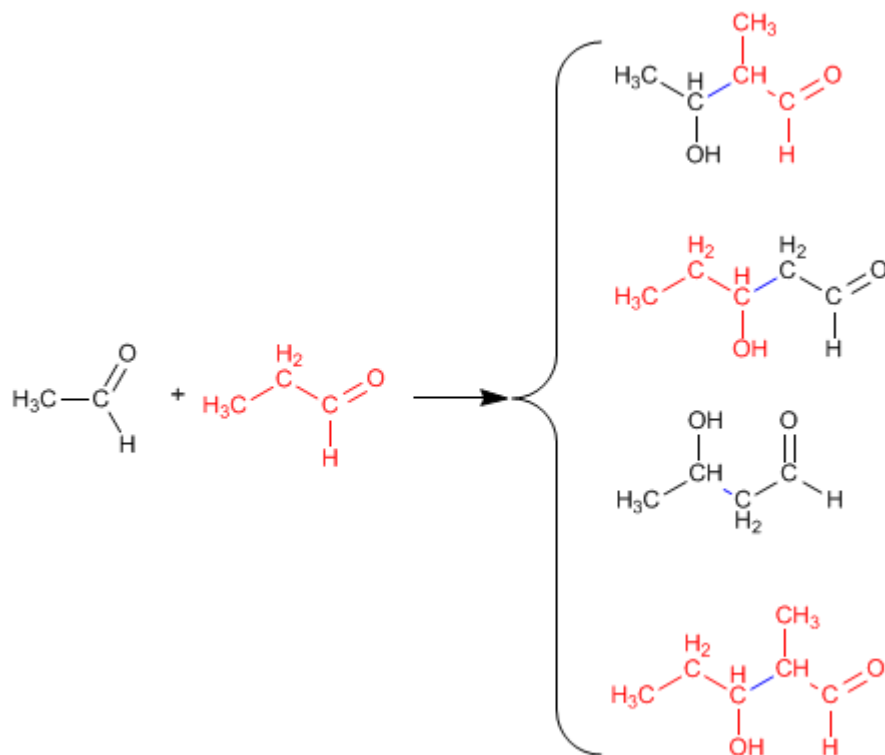


Condensación aldólica cruzada o mixta

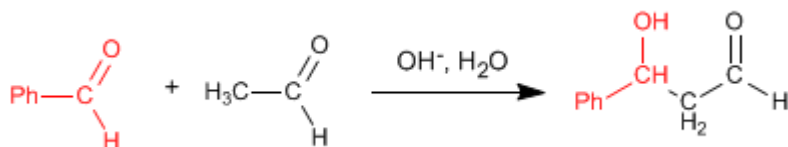
La reacción entre dos carbonilos diferentes se llama aldólica cruzada o mixta. Esta reacción sólo tiene utilidad sintética en dos casos:

1. Sólo uno de los carbonilos puede formar enolatos.
2. Uno de los carbonilos es mucho más reactivo que el otro.

En el resto de situaciones la aldólica mixta genera mezclas de cuatro productos. Veamos como ejemplo la condensación del etanal y propanal.

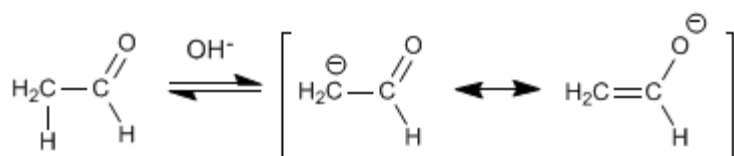


La condensación aldólica mixta del etanal con el benzaldehído genera un producto, cuando se trabaja en exceso de benzaldehído, debido a que el benzaldehído carece de hidrógenos en el carbono alfa y no puede formar enolatos.



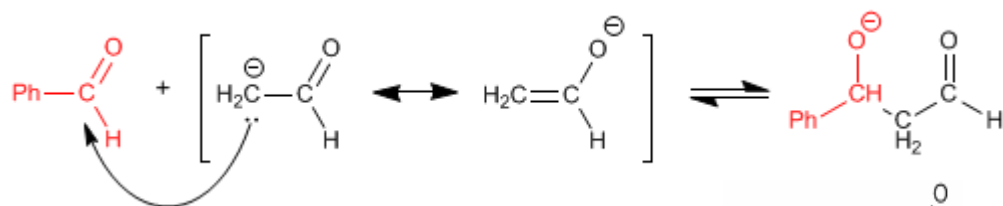
El mecanismo de esta reacción tiene lugar en las siguientes etapas:

Etapla 1. Enolización del etanal

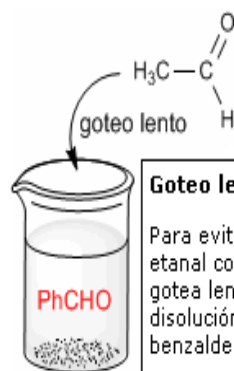
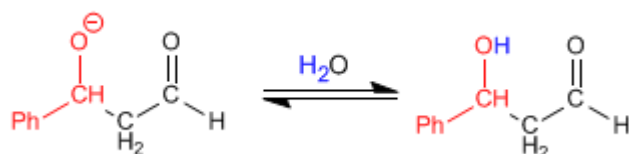


La formación de enolatos sólo puede tener lugar con el etanal, puesto que el benzaldehído carece de hidrógenos ácidos en el carbono alfa.

Etapla 2. Ataque nucleófilo del enolato al benzaldehído.



En esta etapa puede ocurrir el ataque del enolato de etanal sobre si mismo. Para evitarlo debe trabajarse en exceso de benzaldehído. Un procedimiento experimental muy usado para evitar la condensación del etanal consigo mismo es gotear lentamente el etanal sobre una disolución básica de benzaldehído

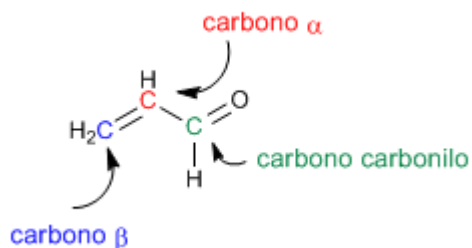


Goteo lento

Para evitar la condensación del etanal consigo mismo, se gotea lentamente sobre una disolución básica de benzaldehído.

Síntesis de carbonilos alfa,beta-insaturados

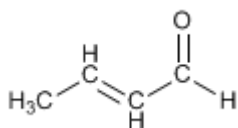
Los carbonilos α,β -insaturados son compuestos orgánicos que tienen un doble enlace entre las posiciones α,β de un aldehído o cetona.



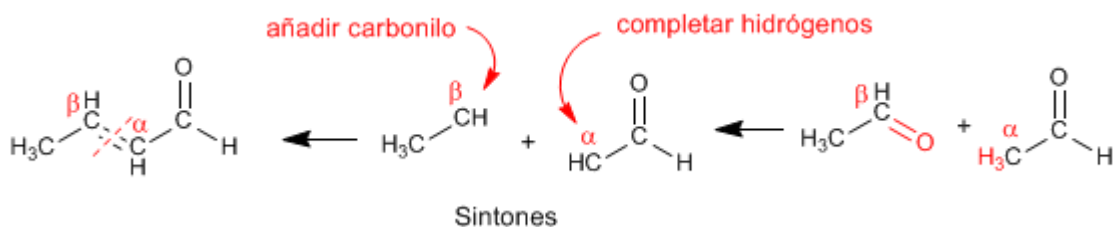
El propenal o acroleína es un carbonilo α,β -insaturado. Sus dos dobles enlaces conjugados le confieren una reactividad especial.

Existen 4 métodos importantes para la preparación de α,β -insaturados: condensación aldólica, halogenación del carbono α seguida de eliminación, oxidación de alcoholes alílicos y Wittig.

Método 1. Preparar mediante la condensación aldólica el siguiente compuesto.

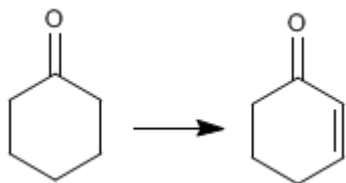


Empleamos la retrosíntesis para preparar el compuesto. Al ser de la familia de los α,β -insaturados se puede obtener mediante la condensación aldólica.

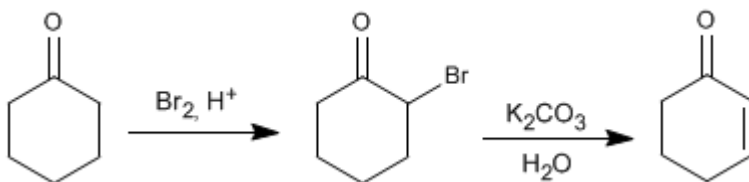


Para obtener los reactivos que forman el α,β -insaturado se rompe por el doble enlace, obteniéndose los sintones (equivalentes sintéticos). Los reactivos se obtienen añadiendo al carbono β un carbonilo y completando los hidrógenos que faltan en el carbono α .

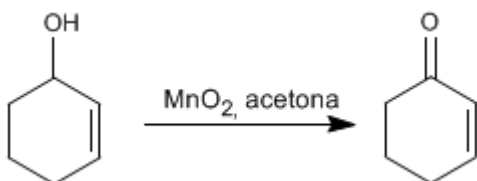
Ejemplo 2. Indicar como se puede realizar la siguiente transformación.



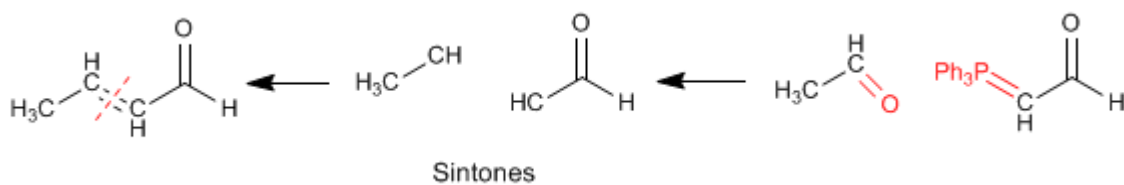
En una primera etapa se halogena la posición α del carbonilo. En la segunda etapa se realiza una eliminación que nos deja el producto final.



Método 3. La oxidación de alcoholes alílicos con dióxido de manganeso en acetona produce α,β -insaturados



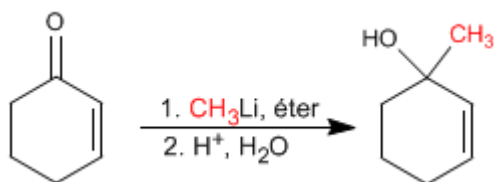
Método 4. Reacción de Wittig



Reactividad de carbonilos alfa,beta-insaturados

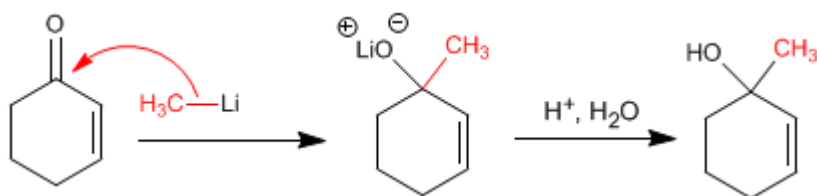
Los α,β -insaturados son compuestos que poseen dos posiciones electrófilas: el carbono carbonilo y el carbono β .

Adiciones 1,2. Los organometálicos de litio atacan al carbono carbonilo dando lugar a adiciones 1,2.



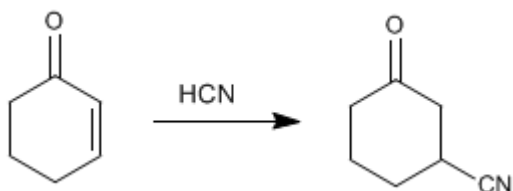
Los organometálicos de litio y magnesio atacan al carbono carbonilo de los α,β -insaturados

Mecanismo de la adición 1,2

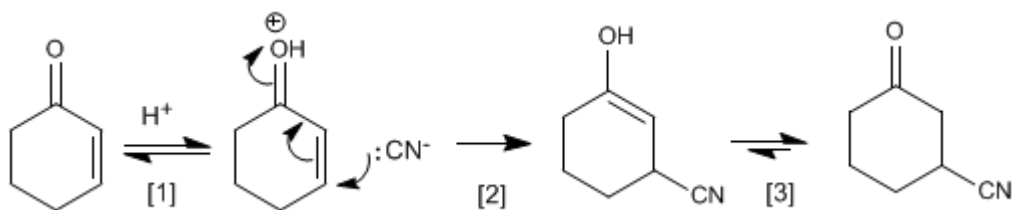


Adiciones 1,4. Los cupratos, cianuro y otros nucleófilos atacan al carbono β de los α,β -insaturados, dando adiciones 1,4.

El ácido cianhídrico da adiciones 1,4 con los α,β -insaturados. El ciano se une al carbono β .

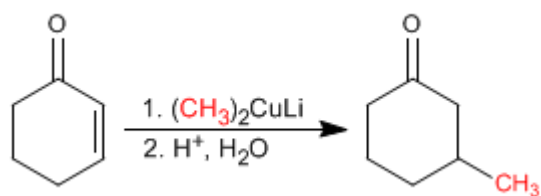


Mecanismo de adición del ácido cianhídrico a la Ciclohex-2-enona

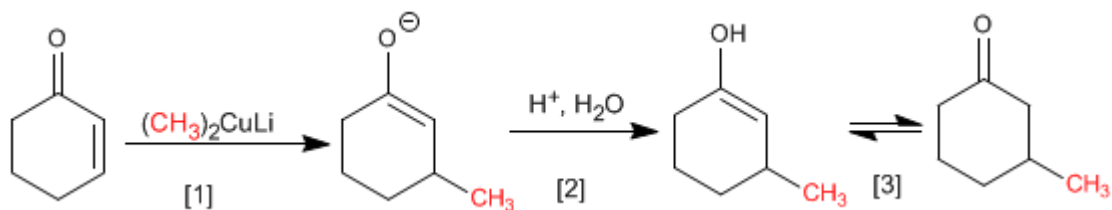


- [1] Protonación del carbonilo
- [2] Ataque nucleófilo del cianuro al carbono β .
- [3] Tautomería ceto-enol.

Los cupratos son organometálicos de cobre que se adicionan al carbono β de los α,β -insaturados.



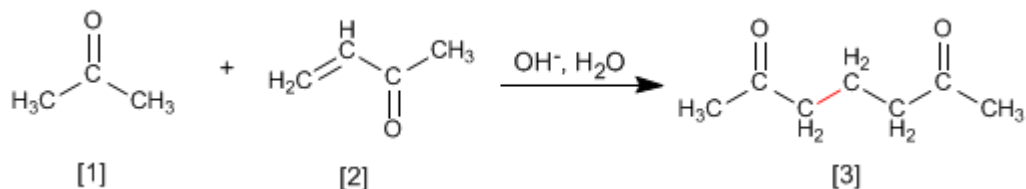
El mecanismo de la reacción comienza con el ataque nucleófilo del cuprato sobre el carbono β , formando un enolato, que se protona en la segunda etapa para dar un enol. El enol tautomeriza a cetona generando el producto final.



- [1] Adición nucleófila del cuprato.
- [2] Protonación del enolato
- [3] Tautomería ceto-enol

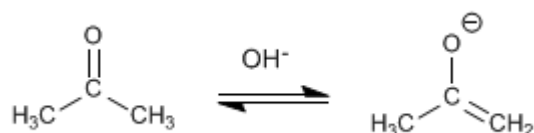
Adición de Michael y anelación de Robinson

Los enolatos de aldehídos o cetonas se adicionan a los α,β -insaturados para formar 1,5-dicarbonilos. Esta reacción se denomina adición de Michael.

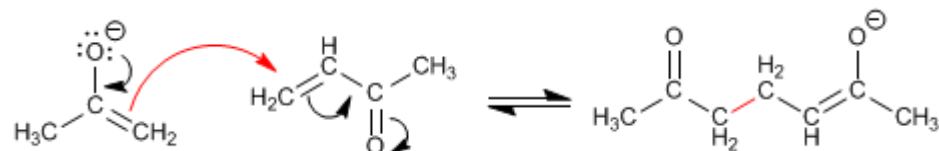


La propanona [1] reacciona con el α,β -insaturado [2] para formar el 1,5-dicarbonilo [3]
Mecanismo de la Adición de Michael:

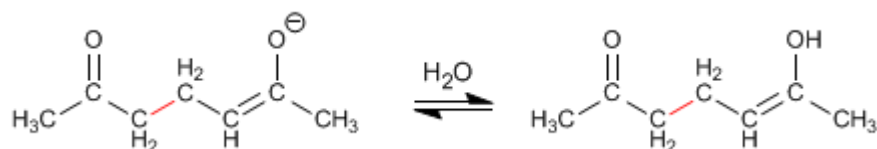
Etapla 1. Formación del enolato.



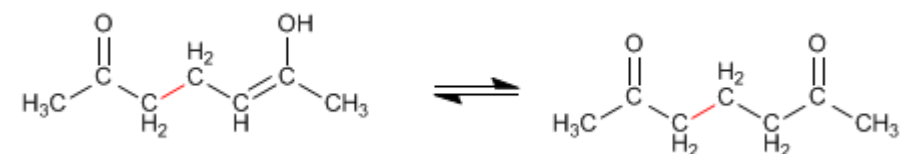
Etapla 2. Ataque nucleófilo del enolato al carbono β del α,β -insaturado.



Etapla 3. Equilibrio ácido-base



Etapla 4. Tautomería ceto-enol

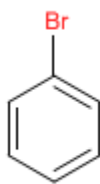


El producto de Michael puede condensar mediante una aldólica intramolecular, formando un α,β -insaturado. El conjunto de la adición de Michael y la aldólica final se conoce como reacción de Robinson

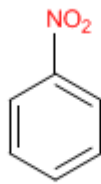
TEORÍA DEL BENCENO

Nomenclatura del Benceno

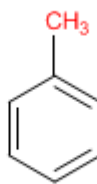
Los bencenos monosustituídos se nombran terminando el nombre del sustituyente en benceno.



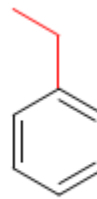
Bromobenceno



Nitrobenceno

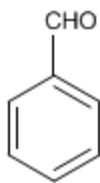


Metilbenceno

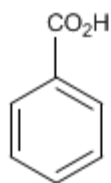


Etilbenceno

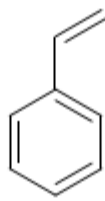
Algunos derivados monosustituídos del benceno tienen nombres comunes ampliamente aceptados.



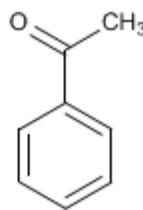
Benzaldehído



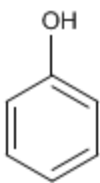
Ácido benzoico



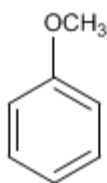
Estireno



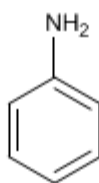
Acetofenona



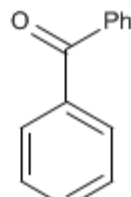
Fenol



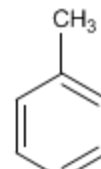
Anisol



Anilina

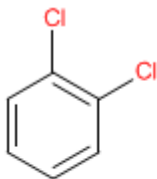


Benzofenona

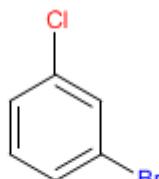


Tolueno

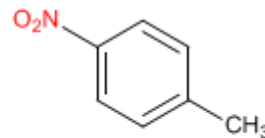
En bencenos disustituídos se emplean los prefijos *orto* (benceno 1,2-disustituído), *meta* (benceno 1,3-disustituído) y *para* (benceno 1,4-disustituído) para indicar la posición de los sustituyentes en el anillo.



o-Diclorobenceno
(1,2-Diclorobenceno)



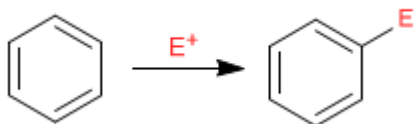
m-Bromoclorobenceno
(1-Bromo-3-clorobenceno)



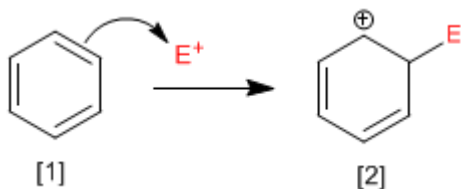
p-Nitrotolueno
(4-Nitrotolueno)

Sustitución Electrónica Aromática

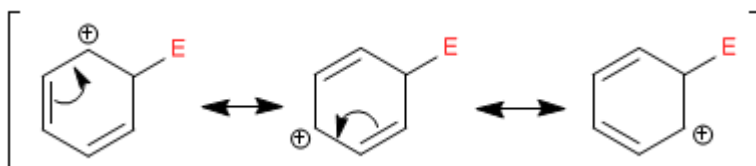
El benceno actúa como nucleófilo, atacando a un número importante y variado de electrófilos.



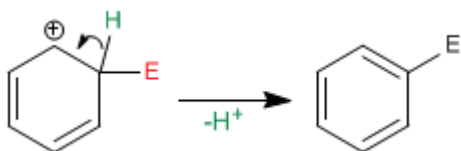
Etapas 1. En la primera etapa de la reacción el electrófilo acepta un par de electrones procedentes de la nube π del benceno, formándose un carbocatión estabilizado por resonancia.



El catión ciclohexadienilo [2] deslocaliza la carga positiva según las siguientes estructuras:

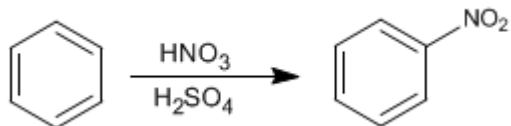


Etapas 2. En la segunda etapa el benceno recupera su aromaticidad por pérdida de un protón. Es una etapa rápida conocida como rearomatización del anillo.

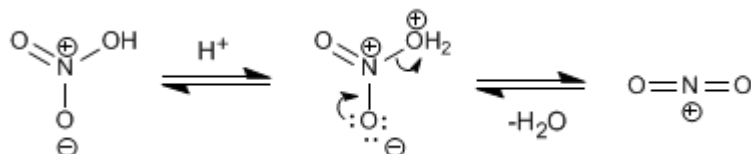


Nitración del Benceno

El benceno reacciona con la mezcla nítrico-sulfúrica adicionando grupos nitro.

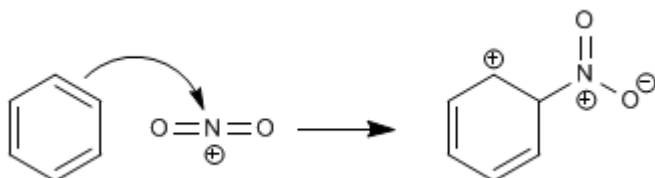


El electrófilo de esta reacción es el catión nitronio, NO_2^+ . Las concentraciones de este catión en el ácido nítrico son muy bajas para nitrar el benceno, por ello es necesario añadir ácido sulfúrico.

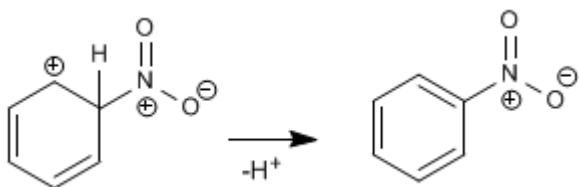


Mecanismo para la nitración del benceno:

Etapla 1. Ataque del benceno al catión nitronio

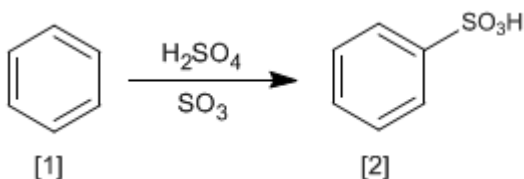


Etapla 2. Recuperación de la aromaticidad por pérdida de un protón



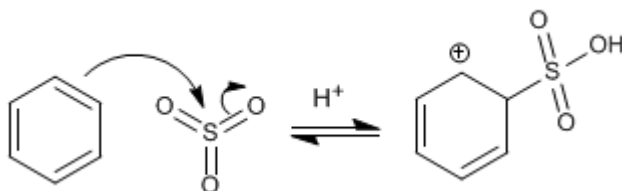
Sulfonación del Benceno

La reacción del benceno [1] con una disolución de trióxido de azufre en ácido sulfúrico produce ácidos bencenosulfónicos [2].

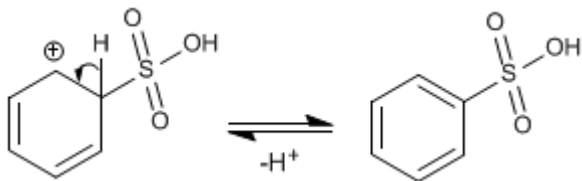


El mecanismo de la sulfonación tiene lugar con las siguientes etapas:

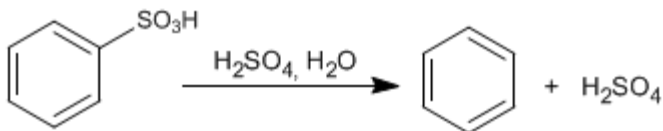
Etapas 1. Ataque del benceno al trióxido de azufre



Etapas 2. Recuperación de la aromaticidad por pérdida de un protón.

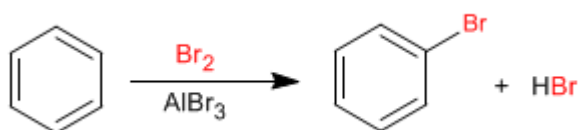


El mecanismo de la sulfonación es reversible, lo cual permite eliminar el grupo $-\text{SO}_3\text{H}$ por tratamiento con sulfúrico acuoso. Esta propiedad es utilizada para proteger posiciones del benceno, ocupándolas con el grupo $-\text{SO}_3\text{H}$.



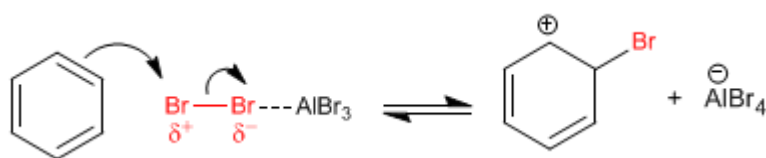
Halogenación del Benceno

El benceno reacciona con halógenos en presencia de ácidos de Lewis para formar derivados halogenados.

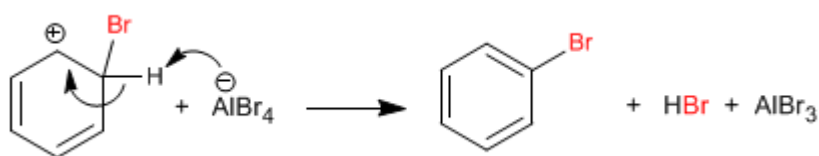


El mecanismo de la halogenación tiene lugar con las siguientes etapas:

Etapas 1. La molécula de bromo se polariza al interactuar con el ácido de Lewis. El benceno ataca al bromo polarizado positivamente para formar el catión ciclohexadienilo.



Etapas 2. Recuperación de la aromaticidad por pérdida de un protón.

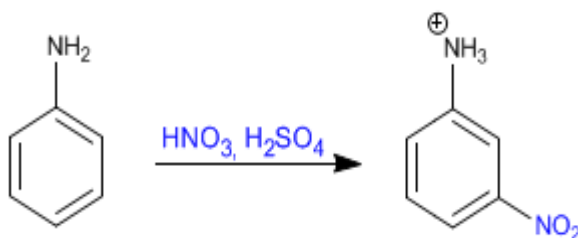


La cloración se puede llevar a cabo de forma similar a la bromación. La reacción con flúor y yodo se realiza muy poco frecuentemente. En el caso del flúor la reacción es difícil de controlar por su elevada reactividad. Por el contrario, el yodo reacciona lentamente y tiene un equilibrio desfavorable.

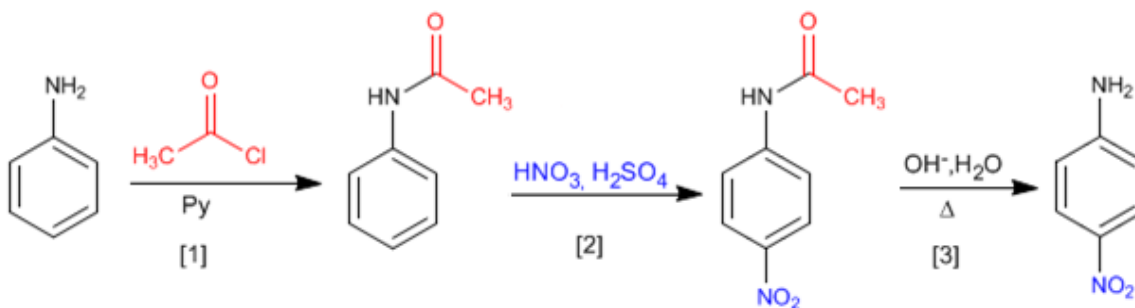
Benceno - Protección y desprotección del grupo amino

El grupo amino es un activante fuerte, que orienta a orto/para. Sin embargo, en medios ácidos se protona transformándose en un desactivante fuerte (sal de amonio) que orienta a posición meta. Se puede evitar la protonación del amino protegiéndolo con cloruro de etanoilo en piridina.

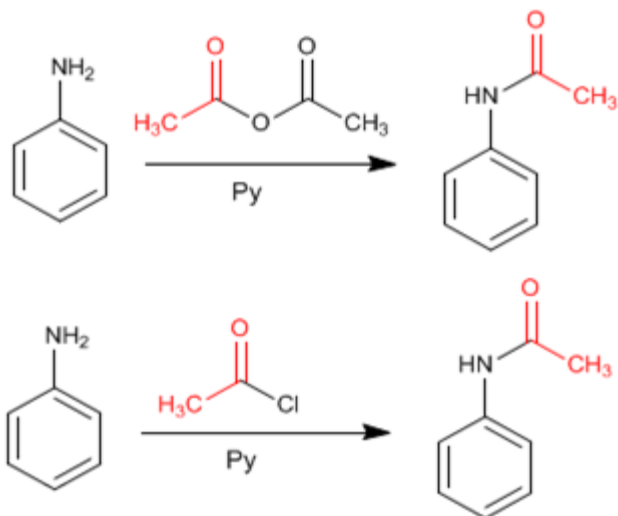
Nitración de la anilina sin protección del amino



Nitración de la anilina con protección del grupo amino, empleando cloruro de etanoilo

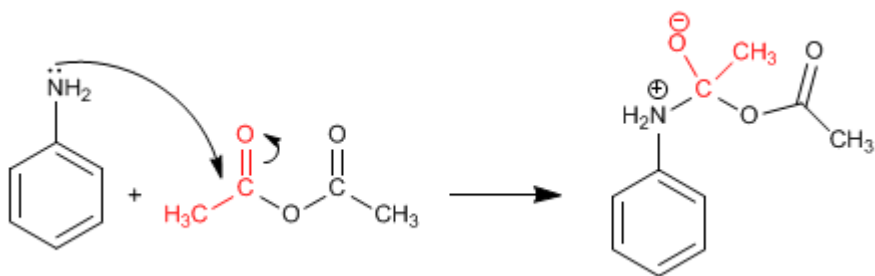


La protección del amino puede realizarse con anhídrido etanoico en piridina, o con cloruro de etanoilo en piridina

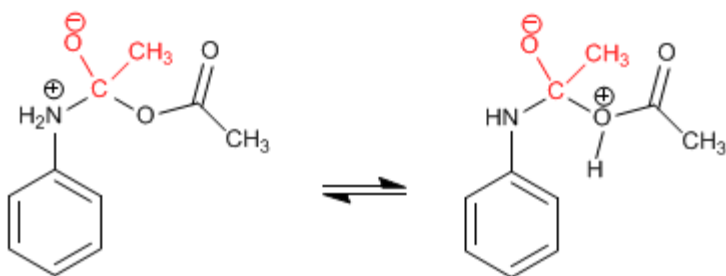


El producto final es una amida, mucho menos básica que la amina de partida y con menos tendencia a protonarse. El mecanismo de la reacción es el siguiente:

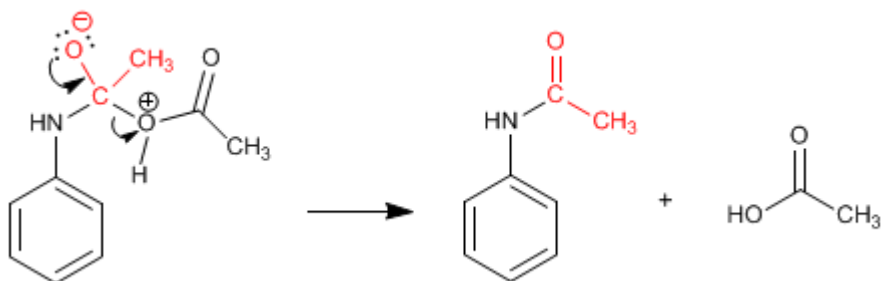
Etapla 1. Adición



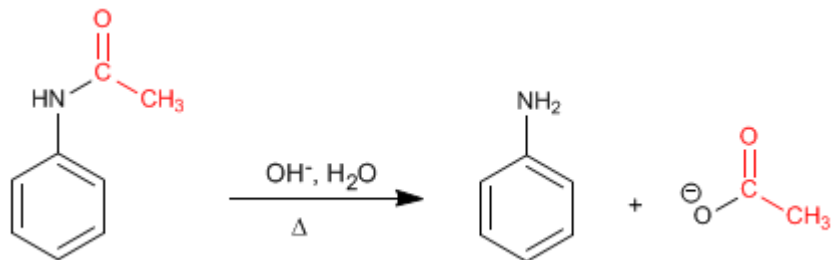
Etapla 2. Equilibrio ácido-base



Etapla 3. Eliminación

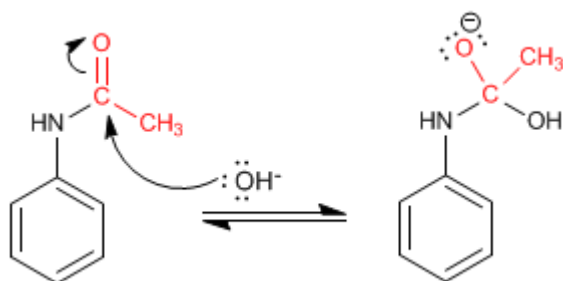


La amida formada se desprotege por hidrólisis ácida o básica, dejando libre la anilina.

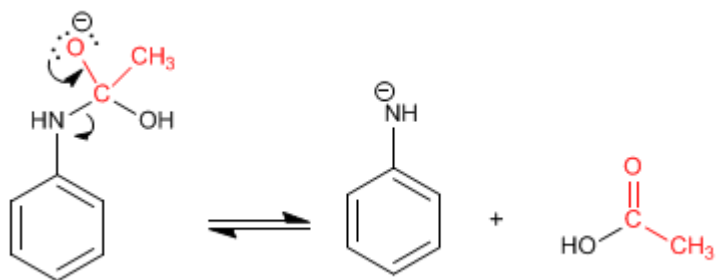


Mecanismo de desprotección en medio básico.

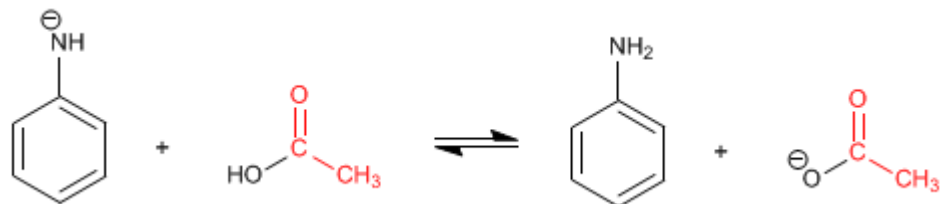
Etapla 1. Adición del grupo hidroxilo a la amida



Etapla 2. Eliminación

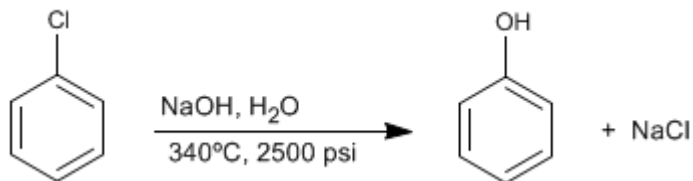


Etapla 3. Equilibrio ácido-base



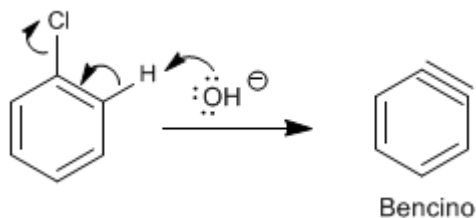
Sustitución nucleófila aromática: Bencino

Los bencenos halogenados reaccionan con sosa diluida en condiciones de alta presión y temperatura, para formar fenoles. Esta reacción no requiere grupos desactivantes en posición orto/para y sigue un mecanismo diferente al de la sustitución nucleófila aromática por adición-eliminación.

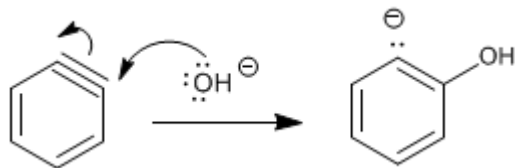


Esta reacción fue descubierta en 1928 por los químicos de la compañía Dow Chemical. El mecanismo consiste en la eliminación de HCl con formación de un intermedio inestable llamado bencino, el cual es atacado por los iones hidróxido del medio, para formar fenol.

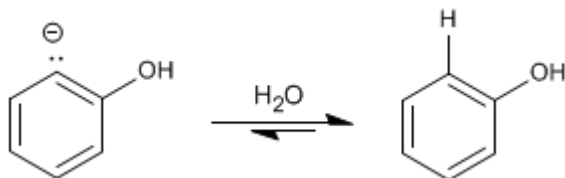
Etapas 1. Eliminación de HCl



Etapas 2. Adición del ion hidróxido al bencino



Etapas 3. Protonación



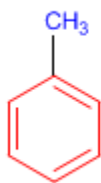
El mecanismo de esta reacción recibe el nombre de sustitución nucleófila aromática por eliminación-adición.

Cuando en el benceno existen sustituyentes produce mezclas, debido al ataque del nucleófilo sobre los dos carbonos del triple enlace.

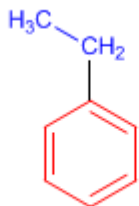
PROBLEMAS NOMENCLATURA - BENCENO

Nomenclatura de Benceno - Reglas IUPAC

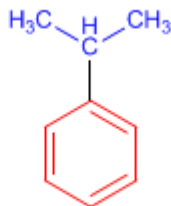
Regla 1. En bencenos monosustituídos, se nombra primero el radical y se termina en la palabra benceno.



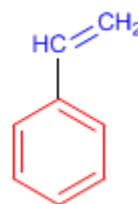
Metilbenceno



Etilbenceno

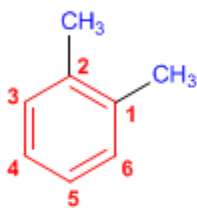


Isopropilbenceno



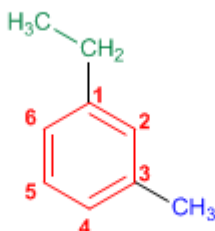
Vinilbenceno

Regla 2. En bencenos disustituídos se indica la posición de los radicales mediante los prefijos *orto-* (*o-*), *meta* (*m-*) y *para* (*p-*). También pueden emplearse los localizadores 1,2-, 1,3- y 1,4-.



o-Dimetilbenceno

(1,2-Dimetilbenceno)



m-Etilmetilbenceno

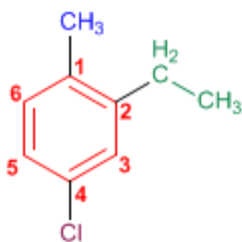
(1-Etil-3-metilbenceno)



p-Isopropilmetilbenceno

(1-Isopropil-4-metilbenceno)

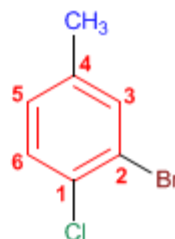
Regla 3. En bencenos con más de dos sustituyentes, se numera el anillo de modo que los sustituyentes tomen los menores localizadores. Si varias numeraciones dan los mismos localizadores se da preferencia al orden alfabético.



4-Cloro-2-etil-1-metilbenceno

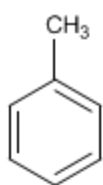


1,4-Dietil-2-metilbenceno

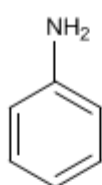


2-Bromo-1-cloro-4-metilbenceno

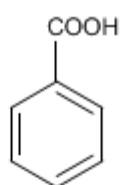
Regla 4. Existen numerosos derivados del benceno con nombres comunes que conviene saber:



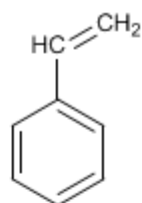
Tolueno



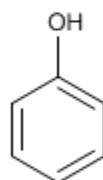
Anilina



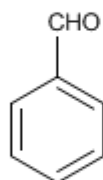
Ac. Benzoico



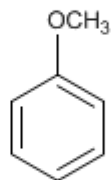
Estireno



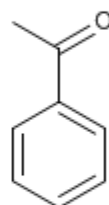
Fenol



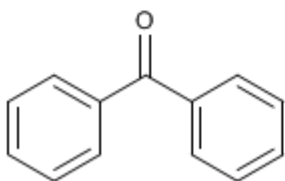
Benzaldehido



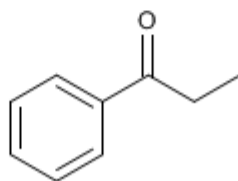
Anisol



Acetofenona



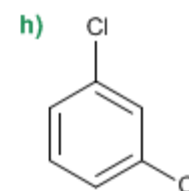
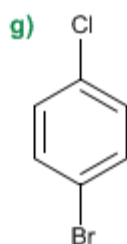
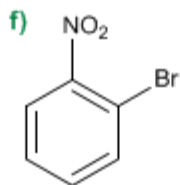
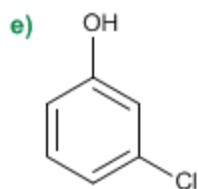
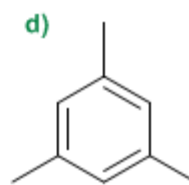
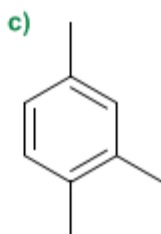
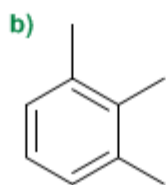
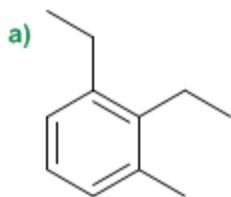
Benzofenona



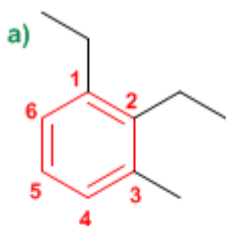
Propiofenona

Nomenclatura de Benceno - Problema 0.1

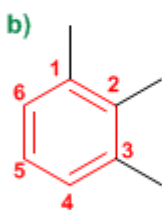
Nombra los siguientes derivados del benceno:



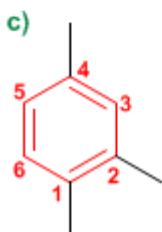
Solución



1. Cadena principal: benceno
2. Numeración: los sustituyentes deben tomar los menores localizadores, y además, se asignan los localizadores menores a los grupos que van antes en el orden alfabético (etilo antes que metilo)
3. Sustituyentes: etilos en 1,2 y metilo en 3.
4. Nombre: 1,2-Dietil-3-metilbenceno



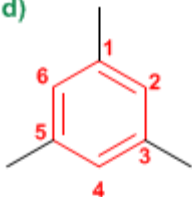
1. Cadena principal: benceno
2. Numeración: los sustituyentes deben tomar los menores localizadores.
3. Sustituyentes: metilos en posición 1,2,3.
4. Nombre: 1,2,3-Trimetilbenceno



1. Cadena principal: benceno
2. Numeración: los sustituyentes deben tomar los menores localizadores.
3. Sustituyentes: metilos en posición 1,2,4.
4. Nombre: 1,2,4-Trimetilbenceno

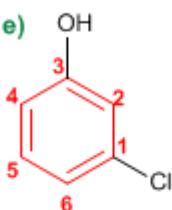
El anillo se numera para que los sustituyentes tomen los localizadores más bajos. En caso de empate se tiene en cuenta el orden alfabético

d)



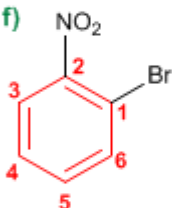
1. Cadena principal: benceno
2. Numeración: se parte de un metilo y se numera en cualquier dirección.
3. Sustituyentes: metilos en 1,3,5.
4. Nombre: 1,3,5-Trimetilbenceno

e)



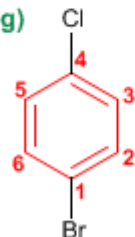
1. Cadena principal: benceno
2. Numeración: la numeración comienza en el cloro (va antes alfabéticamente) y prosigue por el camino más corto hacia el hidroxilo.
3. Sustituyentes: cloro en posición 1 e hidroxilo en posición 3 (posición meta)
4. Nombre: 1-Cloro-3-hidroxibenceno (*m*-Clorohidroxibenceno)

f)



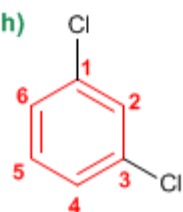
1. Cadena principal: benceno
2. Numeración: la numeración comienza en el bromo (preferencia alfabética)
3. Sustituyentes: bromo en posición 1 y nitro en posición 3 (posición orto)
4. Nombre: 1-Bromo-3-nitrobenzene (*o*-Bromonitrobenzene)

g)



1. Cadena principal: benceno
2. Numeración: comienza en el bromo (preferencia alfabética sobre el cloro)
3. Sustituyentes: bromo en 1 y cloro en 4 (posición para)
4. Nombre: 1-Bromo-4-clorobenceno (*p*-Bromoclorobenceno)

h)



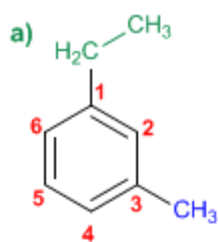
1. Cadena principal: benceno
2. Numeración: localizadores más bajos posibles a los cloros.
3. Sustituyentes: cloros en posición 1,3.
4. Nombre: 1,3-Diclorobenceno (*m*-Diclorobenceno)

Nomenclatura de Benceno - Problema 0.2

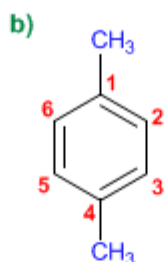
Formular los siguientes derivados del benceno:

- | | |
|---|---|
| a) 1-Etil-3-metilbenceno | k) 4,5-Difenil-1-octeno |
| b) <i>p</i> -Dimetilbenceno | l) 2-Fenil-4-metilhexeno |
| c) 1-Butil-3-etilbenceno | m) 1-(metiletil)-4-(2-metilpropil)benceno |
| d) <i>o</i> -Cloronitrobenceno | n) 6-Fenil-3-metilhexa-1,4-dieno |
| e) <i>m</i> -Bromoclorobenceno | o) <i>cis</i> -1-Fenil-1-buteno |
| f) <i>p</i> -Diisopropilbenceno | p) <i>trans</i> -2-Fenil-2-buteno |
| g) 1- <i>tert</i> -Butil-4-metilbenceno | q) 7-Etil-4,5-difenildec-5-en-1-ino |
| h) <i>o</i> -Alilvinilbenceno | r) <i>m</i> -Diciclohexilbenceno |
| i) <i>m</i> -Etilpropilbenceno | s) <i>p</i> -Ciclobutilciclobutilbenceno |
| j) 2-Etil-1,4-dimetilbenceno | t) 3-(1,1-Difeniletil)-3-metilhex-1-en-5-ino. |

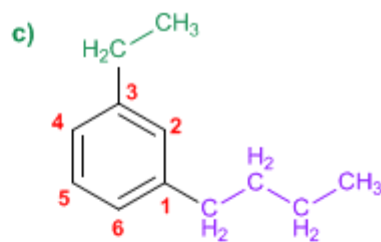
Solución



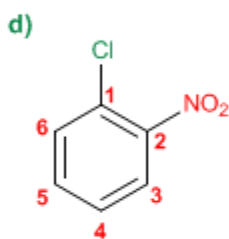
1-Etil-3-metilbenceno



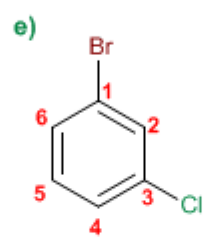
p-Dimetilbenceno



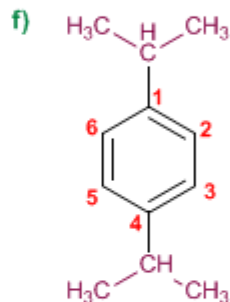
1-Butil-3-etilbenceno



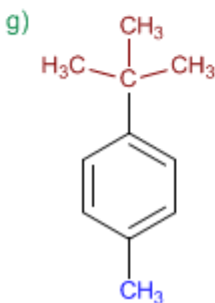
o-Cloronitrobenceno



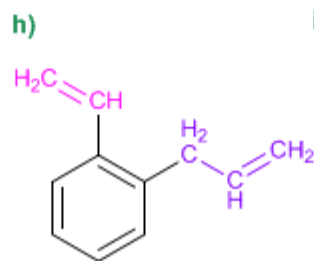
m-Bromoclorobenceno



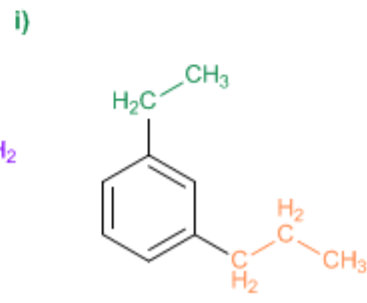
p-Diisopropilbenceno



1-*tert*-Butil-4-metilbenceno

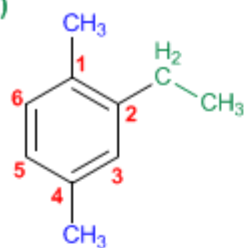


o-Alilvinilbenceno



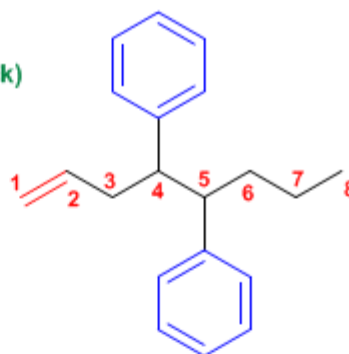
m-Etilpropilbenceno

j)



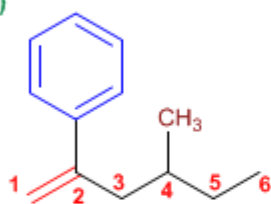
2-Etil-1,4-dimetilbenceno

k)



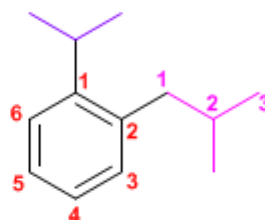
4,5-Difenil oct-1-eno

l)



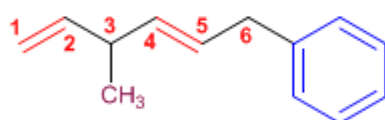
2-Fenil-4-metilhex-1-eno

m)



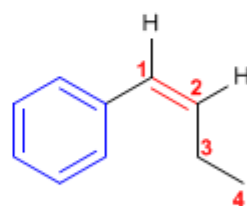
1-(metiletil)-2-(2-metilpropil)benceno

n)

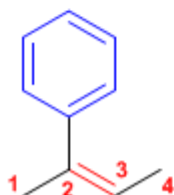


6-Fenil-3-metilhexa-1,4-dieno

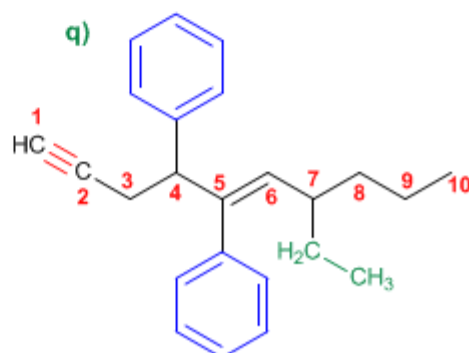
o)

*cis*-1-Fenil-1-butenó

p)

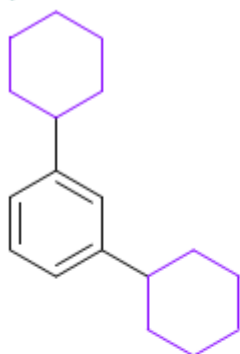
*trans*-2-Fenil-2-butenó

q)



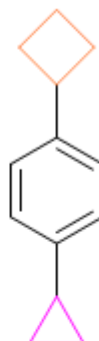
7-Etil-4,5-difenildec-5-en-1-ino

r)



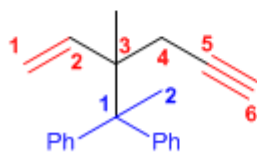
m-Dicyclohexylbenzene

s)



p-Cyclobutylcyclopropylbenzene

t)



3-(1,1-Diphenylethyl)-3-methylhex-1-en-5-yn-3-ol.

Agradecimientos:

❖ <http://www.quimicaorganica.org>

❖ <http://www.taringa.net/perfil/jose07070012>